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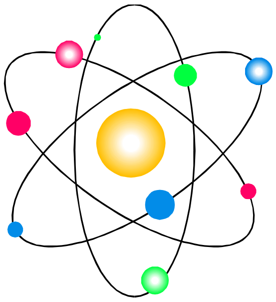

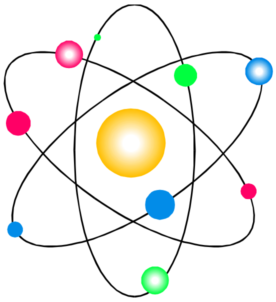

An introductory guide to Gaussian basis sets in solid-state electronic structure calculations[†]

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The purpose of these notes is to provide some insight into Gaussian basis set technology as implemented in the CRYSTAL Hartree-Fock/density functional theory program for periodic systems[1]. Essential differences between basis sets appropriate for use in solids and those used in purely molecular codes are explained. Examples of how to choose appropriate basis sets for particular problems, hints on basis set development, and some simple exercises are also included.

1. Basis set expansions

In order to calculate molecular or crystalline structures and properties, it is necessary to determine the eigenfunctions Ψ and eigenvalues E of the Schrödinger equation

$$\hat{H}\Psi = E\Psi. \tag{1.1}$$

where $\hat{H}$ is the electronic Hamiltonian. For systems of interest in chemistry, analytic solutions to this problem are impossible to find, and so one normally resorts to the *variational approach* involving the introduction of a trial wave function $\overline{\Psi}(\alpha)$ that depends on a set of variable parameters $\{\alpha\}$. If the functional

$$\overline{E}(\alpha) = \frac{\langle\overline{\Psi}|\hat{H}|\overline{\Psi}\rangle}{\langle\overline{\Psi}|\overline{\Psi}\rangle} \tag{1.2}$$

is minimized with respect to variations in $\{\alpha\}$, the energy converges from above on the true energy in (1.1), and the wave function converges in the mean on the true wave function as the parameter set $\{\alpha\}$ is expanded to completeness.

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The most obvious way of implementing this approach is to make the trial wave function depend linearly on the parameters $\{\alpha\}$. The resulting linear expansion may be written most generally as

$$\overline{\Psi} = \sum_{\mu} \Phi_{\mu} c_{\mu} . \tag{1.3}$$

A set of equations for the linear coefficients c_μ in this expansion may be derived on substitution of (1.3) into (1.2) by making the energy stationary with respect to variations in the coefficients. The *N-particle basis functions* $\{\Phi\}$ are a set of fixed analytic functions that depend on the co-ordinates of *all* electrons in the system. They can conveniently be taken to be orthonormal, in which case the variational equations correspond to the eigenvalue problem

$$\mathbf{Hc} = E\mathbf{c} . \tag{1.4}$$

If the N-particle basis were a complete set of N-electron functions, the use of the variational approach would introduce no error, because the true wave function could be expanded exactly in such a basis. However, the basis would then be of infinite dimension, and in practice, the fact that we must work with an incomplete set of N-particle functions is one of our major practical approximations. Furthermore, the question arises of how to construct the N-particle basis itself. There are many possible physically motivated ways of doing this, but in most practical quantum chemistry techniques it is constructed using linear combinations of products of *one-electron wave functions* or *orbitals.* These are usually antisymmetrized to account for the permutational symmetry of the wave function (and may also be spin and symmetry adapted):

$$\Phi_{\mu} = \hat{A} \prod_{i}^{N} \phi_{\mu i}(x_i) \tag{1.5}$$

Here $\hat{A}$ is an antisymmmetrization operator and the x_{i} are the space and spin co-ordinates of a single electron. In this form the N-particle basis functions are called *Slater determinants.* The unknown one-electron functions $\{\phi\}$ in (1.5) are referred to as *atomic*, *molecular* or *crystalline orbitals* depending on the physical nature of the problem. To find the unknown orbitals, one generally expands them as an orthonormal linear combination of known one-electron basis functions χ_a:

$$\phi_{\mu i} = \sum_{a} \chi_a C_{a,\mu i} \tag{1.6}$$

One then obtains a set of algebraic equations for the optimum orbitals which may be solved by standard matrix techniques. The set of functions $\{\chi\}$ in (1.6) constitute the one-particle basis set given as input to most quantum chemistry calculations. This is what these notes are about.

So evidently the simplest truncation of the N-particle space is that in which only one N-electron basis function is used - a single configuration which is the best variational approximation to the exact ground-state wave function. In this case all coefficients in the expansion (1.3) are zero with the exception of that of the ground-state configuration. Minimizing the expectation value of the Hamiltonian with respect to the one-electron orbitals in a single determinant trial function allows us to derive the self-consistent Hartree-Fock (HF) equations, which may be solved to find the optimum orbitals (i.e. the best coefficients of equation (1.6)). To develop 'correlated wave function methods' that give a better description of electron-electron correlation than HF one usually uses more complex techniques involving combinations of explicitly many-particle functions such as, for example, configuration interaction (CI)[2], MC-SCF[3] or coupled-cluster[4] methods (although stochastic techniques such as *quantum Monte Carlo* are becoming an increasingly poplar alternative – see later). The HF special case is sufficiently important that the difference $E_{exact} - E_{HF}$ is defined as the *correlation energy*. Here E_{HF} is the Hartree-Fock energy, that is, the SCF result in a complete one-particle basis set. The *Hartree-Fock limit* is thus defined as the complete one-particle space single-configuration result.

Of course, an excellent and generally cheaper alternative to wave function methods is Kohn-Sham *density functional theory* (KS-DFT). In this scheme the single determinant of orbitals is not meant to represent the true many-electron wave function as in HF theory. The basic idea of the Kohn-Sham scheme is to replace the calculation of the true wave function Ψ by that of a single Slater determinant that represents a non-interacting model system and yields the same ground state density as Ψ. However the expectation value of the Hamiltonian with this determinant only gives part of the total energy. The remaining (exchange-correlation) contribution to the total energy is not directly accessible by the determinant and is given by an (approximate) functional of the total density. Pretty much all statements here concerning the one-particle basis set are applicable both to HF and Kohn-Sham orbitals, but where there are distinctions these will be noted.

The nature of the one-particle basis functions used in in the expansion of the orbitals depends on the periodicity of the system. In the molecular case, functions localized at the nuclear centres are generally used, consisting of products of a radial function $R(r)$ (such as a Gaussian) and an angular function (such as a spherical harmonic $Y_{lm}(\theta,\phi)$). In the periodic case by contrast, the one-particle basis must be made up of *Bloch functions* $\tilde{\chi}_{i\mathbf{k}}(\mathbf{r})$ i.e. products of a function periodic in the primitive lattice and a phase factor whose frequency and direction of oscillation is dependent on the wave vector **k**. These Bloch functions might be, for example. simple plane-waves $\exp(i(\mathbf{k}+\mathbf{G}).\mathbf{r})$, where **G** is a vector in the reciprocal lattice, or as in CRYSTAL a combination of a localized function χ_a and all of its periodic images with the whole modulated by a phase factor:

$$\tilde{\chi}_{i\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{t}} \chi_a^{\mathbf{t}}(\mathbf{r} - \mathbf{r}_a - \mathbf{t}) \exp(i\mathbf{k}\cdot\mathbf{t}) \tag{1.7}$$

Here $\chi_a^{\mathbf{t}}$ refers to the *a*th localized atomic function (lying at position $\mathbf{r}_a$ in the zero cell) in the unit cell of the crystal described by the lattice translation vector **t**. Note that because the wave vector **k** is a continuous variable, the basis set of Bloch functions is in principle infinite; in practice however, the problem is solved at a finite set of **k** points, and the results interpolated.

Thus the one-particle basis of atomic functions/Bloch functions determines the one-particle orbitals, which in turn determine the *N*-particle basis. If the one-particle basis were complete, it would in principle be possible to form a complete *N*-particle basis, and hence to obtain an exact wave function variationally. Again however, such a complete one-particle basis would be of infinite dimension, and thus the basis must be truncated in practical applications. We must therefore use truncated *N*-particle spaces that are constructed from truncated one-particle bases. These two truncations (i.e. correlation and basis set error) are the most important sources of uncertainty in quantum chemical calculations. It is interesting to note at this point that if we remove the restriction of analytic integrability of basis functions in correlated wave function methods, it is possible to construct much more efficient *N*-particle functions by including terms which depend explicitly on the interparticle distances. A good example is the *Slater-Jastrow* form used in *quantum Monte Carlo* calculations where a single *N*-electron function is usually an excellent approximation to the true wave function and gives a very accurate description of the electron correlation. Such calculations will be the subject of my second lecture at this school but will not be mentioned further here.

It should be noted that the ultimate accuracy of any calculation, in correlated calculations over many *N*-particle basis functions as well as at the SCF level, is determined by the one-particle basis set. This is one of the most obvious observations about quantum chemical calculations, but worth emphasizing nonetheless. It is in general just not possible to get the right answer for the right reason using, for example, an STO-3G Gaussian basis set (see later). This is not necessarily an argument against using such sets (people make bigger approximations every day) but their limitations must be kept constantly in mind. Probably one of the most important lessons of this school is that the choice of one-particle space is *the* most important decision in setting up any calculation, since ultimately this choice determines the reliability of the result. Nothing can overcome limitations in the one-particle basis[†].

In the next section we shall examine particular properties of the one-electron basis functions most commonly used in modern molecular quantum chemistry codes, namely contracted Gaussian-type functions, and how these are modified in a periodic code such as CRYSTAL.

2. One-electron basis sets constructed from Gaussian-type functions

General considerations

Having worked for the last four years in the spiritual home of plane-wave pseudopotential calculations (the Theory of Condensed Matter Group in the Cavendish Laboratory at the University of Cambridge), it has been rather obvious to me that the traditional basis for construction of the one-electron Bloch functions in solid-state electronic structure calculations has *not* been Gaussians. Indeed, you may as well learn now that in certain circles the derision invited by doing so can be tiresome. Chemists are no problem. But if you plan to interact with physicists and to use Gaussian basis sets, it is as well to have rehearsed the arguments for and against beforehand. Referring to what CRYSTAL does as an ‘all-electron full potential LCGTF method’ rather than ‘Gaussian basis set calculations’ will help at first. Do not use the phrase ‘linear combination of atomic orbitals’ under any cirumstances. When pressed, follow the example of the director of this school at a conference some years ago in reference to a question about why he used Hartree-Fock theory (which is quoted to me every time I mention in conversation who I used to work for) and claim

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[†] Except, magically, diffusion Monte Carlo!

that 'it is some strange kind of sexual perversion'. Of course all different basis sets have their advantages and disadvantages. The choice of one set over another is one of personal taste (what codes do I have on my computer that I know how to use?) and a careful consideration of the pros and cons of the various methods (do I want speed, accuracy, forces etc.?). A short discussion along these lines will appear at the end of this section.

So anyway in periodic systems as in molecules the fundamental idea behind the use of localized Gaussian-type functions is the 'atoms in molecules' concept (i.e. molecules are an assemblage of slightly perturbed atoms), and our consequent expectation that localized atomic functions will prove suitable as an expansion set in molecules is generally well-founded. The historical phrase *linear combination of atomic orbitals* is often used to describe this procedure but this is both archaic and inaccurate and should be avoided. Strictly speaking, 'atomic orbitals' are solutions of the Hartree-Fock equations for the atom i.e. a wave function for a single atomic electron in a self-consistent field. Localized basis functions are thus not atomic orbitals, but can in spherical polar coordinates be any function of the form $R(r)\Theta(\vartheta)\Phi(\phi)$ with properties chosen for computational convenience. The equations determining the form of the radial functions $R(r)$ can be solved only for one-electron 'hydrogen-like' atoms, but some general conclusions about the nature of the solutions can still be drawn. In particular, due to the singularity of the potential at a point nucleus with a charge of +*Z*, the wave function must have a 'cusp' at the nucleus. In fact, for such a one-electron atom, it is required that

$$\left.\frac{dR}{dr}\right|_{r=0} = -Z \tag{2.2}$$

At the other end of the range, an electron far away from any molecule would see the remainder of the molecule as a positive charge without any particular structure. Like any one-electron atom, the wave function would therefore decay exponentially. It would thus seem reasonable to use exponential functions as basis functions, especially since they are known to be exact solutions for any one-electron system. Historically therefore, basis functions with exponential asymptotic behaviour - Slater-type orbitals (STOs) - were the first to be used[5]. These are characterized by an exponential factor in the radial part:

$$\chi^{STO} = r^{n-1}\exp(-\zeta r)Y_{lm}(\theta,\phi) \tag{2.3}$$

where ζ ('*zeta*') is called the exponent, the $Y_{lm}(\theta,\phi)$ is the spherical harmonic or angular momentum part (the function describing the 'shape' of the STO), and the *n,l,m* are quantum numbers.

Unfortunately such functions are not suitable for fast calculations of multi-centre integrals, so Gaussian-type functions (GTFs) were introduced to remedy the difficulties Transforming from a local polar coordinate system to a Cartesian one, these can be written

$$\chi^{GTF} = \exp(-\alpha r^2)x^l y^m z^n \tag{2.4}$$

where α is again the exponent, and the *l*,*m*,*n* are not quantum numbers but simply integral exponents of Cartesian coordinates. In this form (now called *Gaussian primitives*) they be factorized into their Cartesian components i.e.

$$\chi^{GTF} = \chi_x^{GTF} \chi_y^{GTF} \chi_z^{GTF} \tag{2.5}$$

where each Cartesian component has the form (introducing an origin such that the Gaussian is located at position x_a),

$$\chi_x^{GTF} = (x - x_a)^l \exp\left(-\alpha (x - x_a)^2\right) . \tag{2.6}$$

This simplifies considerably the calculation of integrals. (It should be clear that if write the exponential part of an STO, $\exp(-\alpha|\mathbf{r}|)$, in Cartesian components we get $\exp\left(-\alpha\sqrt{x^2 + y^2 + z^2}\right)$ which is not so separable). Note that the absence of the STO pre-exponential factor r^{n-1} restricts single Gaussian primitives to approximating only 1*s*, 2*p*, 3*d* etc. orbitals and not e.g. 2*s*, 3*p*, 4*d* etc... However, combinations of Gaussians are able to approximate correct nodal properties of atomic orbitals if the primitives are included with different signs. The sum of exponents of Cartesian coordinates $L = l + m + n$ is used analagously to the angular momentum quantum number for atoms to mark Gaussian primitives as *s*-type (L=0), *p*-type (L=1), *d*-type (L=2), *f*-type (L=3) etc.[†]

The present success of GTFs as the basis set of choice in virtually all molecular quantum chemistry calculations was far from obvious originally. In particular, it is clear that the behaviour of a Gaussian is qualitatively wrong both at the nuclei and in the long-distance limit for a Hamiltonian with point-charge nuclei and Coulomb interaction. It has therefore been a commonly held belief that STOs would be the preferred basis if only the integral evaluation problem could be solved. It has been claimed[6] that this is not necessarily the case and that the 'cusp' behaviour represents an idealized point nucleus, and for more realistic nuclei of finite extension the Gaussian shape may actually be more realistic. If accurate solutions for a point-charge model Hamiltonian are desired, they can be obtained to any desired accuracy in practice by expanding the 'core' basis functions in a sufficiently large number of Gaussians to ensure their correct behaviour. Furthermore, properties related to the behaviour of the wave function at or near nuclei can often be predicted correctly, even without an accurately 'cusped' wave function[7]. In most molecular applications the asymptotic behaviour of the density far from the nuclei is considered much more important than the nuclear cusp. As mentioned above, the wave function for a bound state must fall off exponentially with distance, whenever the Hamiltonian contains Coulomb electrostatic interaction between particles. However, even though an STO basis would in principle be capable of providing such a correct exponential decay, this occurs in practice only when the smallest exponent in the basis set is $\zeta_{\min} = \sqrt{2I_{\min}}$, where $I_{\min}$ is the first ionization potential. Such a restriction on the range of exponent values, while acceptable for atomic SCF calculations, is far too restrictive for

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[†] Note CRYSTAL specifics: CRYSTAL98 allows Gaussian primitives of *s*,*p* or *d* types. In principle, the following six angular functions are possible for Cartesian Gaussians: 1*s* (1), 2*p* (*x*,*y*,*z*), 3*d* (x^2, *xy*, *xz*, *yz*, y^2, z^2). Note that there are only five linearly independent and orthogonal atomic *d* orbitals so internally CRYSTAL uses appropriate linear combinations of Cartesian Gaussians to give the five real spherical harmonic *d* basis functions: $3z^2$-r^2 , *xz*, *yz*, x^2-y^2, *xy* (stored internally in that order).

molecular and solid-state work. Some of these formal limitations have thus turned out to be of relatively little importance in practice. Indeed the universality of Gaussian functions in molecular quantum chemistry is virtually complete - Slater-type functions are hardly used today and we shall not discuss them here any further. Much *more* important are limitations arising from the convergence of results with the size of the basis set.

Contraction schemes

Both the number of integrals over basis functions to be stored on disk and the total CPU time nominally scale rather unpleasantly with the number of functions in the basis set. Thus it usually pays to consider the issue of basis set compactness, that is, the ability to expand the orbitals as accurately as possible using the minimum number of basis functions. Furthermore, although we wish to perform this expansion in terms of localized 'atomic-orbital'-like functions, we have seen that our basis functions of choice (Gaussians) do not in themselves resemble exact HF atomic orbitals particularly closely. In most applications therefore, Gaussian-type basis functions are expanded as a linear combination (or 'contraction') of individually normalized Gaussian primitives $g_j(\mathbf{r})$ characterized by the same centre and angular quantum numbers, but with different exponents,

$$\chi_i(\mathbf{r}) = \sum_{j=1}^{L} d_j g_j(\mathbf{r})$$

$$\text{where} \qquad (2.7)$$

$$g_j(\mathbf{r}) \equiv g(\mathbf{r};\alpha,l,m) = N_{lm}(\alpha) r^l Y_{lm}(\theta,\phi)\exp(-\alpha_j r^2)$$

where L is the length of the contraction, the α_j are the *contraction exponents*, the d_j *contraction coefficients* and I have now written the Gaussian primitives in terms of real spherical harmonics including a normalization constant. By proper choice of these quantities, the 'contracted Gaussians' may be made to assume any functional form consistent with the primitive functions used. One may therefore choose the exponents of the primitives and the contraction coefficients so as to lead to basis functions with desired properties, such as reasonable cusp-like behaviour at the nucleus (e.g. approximate Slater functions or HF atomic orbitals). Integrals involving such basis functions reduce to sums of integrals involving the Gaussian primitives. Even though many primitive integrals may need to be calculated for each basis function integral, the basis function integrals will be rapidly calculated provided the method of calculating primitive integrals is fast, and the number of orbital coefficients in the wavefunction will have been considerably reduced.

The exponents and contraction coefficients are normally chosen on the basis of relatively cheap atomic SCF calculations so as to give basis functions suitable for describing exact Hartree-Fock atomic orbitals. An approximate atomic basis function, whose shape is suitable for physical and chemical reasons, is thus expanded in a set of primitive Gaussians, whose mathematical properties are attractive from a computational point of view. Note that the physical motivation for this procedure is that, while many primitive Gaussian functions may be required to provide an acceptable representation of an atomic orbital, the relative weights of many of these primitives are almost unchanged when the atoms are formed into molecules or crystals. The relative weights of the primitives can therefore be fixed from a previous calculation and only the overall scale factor for this contracted Gaussian function need be determined in the extended calculation. It is clear that contraction will in general significantly reduce the number of basis functions. For example a so-called STO-3G basis, where three Gaussian primitives are used to form a contracted function which resembles a Slater-type orbital, the reduction in size from the primitive basis is a factor of 3, corresponding to a nominal reduction factor of 81 (N^4) on the number of two-electron integrals - clearly a significant reduction.

How does this scheme transfer to the solid state? A finite number p of GTFs, constructed from contractions of Gaussian primitives, are attributed to each of the non-equivalent atoms in the reference zero cell. The same GTFs are then formally associated with all N translationally equivalent atoms in the crystal by direct translations of the lattice vectors **t**. This gives a total of Np GTFs from which Np Gaussian-type Bloch functions (GTBF) are then constructed according to

$$\tilde{\chi}_{a\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{t}} \chi_a(\mathbf{r} - \mathbf{r}_a - \mathbf{t}) \exp(i\mathbf{k} \cdot \mathbf{t})\,. \tag{2.8}$$

where the $\mathbf{r}_a$ are the co-ordinates of the basis atom in the reference zero cell with which χ_a is associated. In fact, for solid-state calculations, there are no practical differences in the form of the basis set input compared to the molecular case, as the transformation of the one-electron basis functions to their Bloch form is done internally after the definition of the localized atomic functions. However, the exponents and contraction coefficients in the two cases will generally be rather different, and with some exceptions such as molecular crystals and certain covalent systems, molecular basis sets are not directly transferable to the study of crystalline solids. We shall return to this point in the next section.

Two further points may be made with respect to basis set contraction schemes. The first concerns the way AOs belonging to a given atom are grouped into *shells*. In general, a shell contains all functions characterized by the same n and l quantum numbers (e.g. all the different d functions in a 3d shell); this allows the partitioning of the total charge density into 'shell charge distributions' and is useful in the selection of bielectronic integrals and in the evaluation of long-range interactions. A feature of the contraction schemes originally used in basis sets of the Pople type (and often useful in calculations with CRYSTAL) is the additional grouping of AOs with only the same principle quantum number into shells; e.g. a 2*sp* shell, in which both 2*s* and 2*p* functions have the same set of exponents α_j but different contraction coefficients d_j. This procedure reduces the number of auxiliary functions to be calculated in the evaluation of electron integrals. In fact basis sets with *sp* shells can give a saving factor as large as four in the CPU time, compared with the case where *s* and *p* have different exponents. Note that CRYSTAL is restricted to *s*, *p* and *d* basis functions and that only *sp* shells may be formed in this way. One should note however, that while the use of *sp* shells may reduce the computational effort somewhat, in certain circumstances it may actually represent an important constraint on the form of the basis functions. For relatively small calculations where the time and storage limitations are not an important factor, some consideration should be given to describing the *s* and *p* functions with separate sets of exponents.

The second point is not directly relevant to the CRYSTAL program but may be encountered in the literature and as such one should be aware of it, namely the so-called *general contraction* scheme[8]. Most standard codes such as CRYSTAL use what is known as a *segmented contraction*, in which the transformation from the larger primitive set to the smaller contracted set is restricted in such a way that each Gaussian primitive g_j contributes to exactly one contracted GTF. The algorithms involved are relatively simple if the transformation is reduced to a series of small, independent summations within mutually exclusive sets. In contrast, the general contraction scheme makes no such assumptions, and allows each Gaussian primitive to contribute to several contracted GTFs. A considerable advantage of the general scheme is that the contracted GTFs reproduce exactly the desired combinations of primitive functions. For example, if an atomic SCF calculation is used to define the contraction coefficients in a general contraction, the resulting minimal basis will reproduce the SCF energy obtained in the primitive basis. This is not the case with segmented contractions. There are other advantages with a general contraction: for example, it is possible to contract inner-shell orbitals to single functions with no error in the atomic energy, making calculations on heavy elements much easier. Another advantage is a conceptual one: using a general contraction, it is possible to perform calculations in which the one-particle space *is* a set of atomic orbitals, a true LCAO scheme, rather than being a segmented grouping of a somewhat arbitrary expansion basis. The MOs can then be analysed very simply, just as for the original qualitative LCAO MO approach, but in terms of 'exact AOs' rather than relatively crude approximations to them.

Computational aspects

One of the most attractive features of Gaussian basis functions is their separability into Cartesian components, as in (2.5). This allows a computationally efficient transition from the spherical symmetry of the atom, naturally represented in a polar co-ordinate system, to a more general Cartesian representation which is useful for describing molecular/crystalline geometries. Another equally important reason for the usefulness of a Gaussian basis set is embodied in the Gaussian product theorem (GPT), which in its simplest form states that the product of two simple Gaussian functions with exponents α and β, located at centres **A** and **B**, is itself a simple Gaussian with exponent γ, multiplied by a constant factor F, located at a point **C** along the line segment **A–B**, where

$$\gamma = \alpha + \beta \tag{2.9a}$$

$$\mathbf{C} = \left(\frac{\alpha \mathbf{A} + \beta \mathbf{B}}{\gamma} \right) \tag{2.9b}$$

$$F = \exp\left(-\frac{\alpha\beta}{\gamma} (\mathbf{A} - \mathbf{B})^2 \right) \tag{2.9c}$$

The product of two *polynomial* GTF, of degree μ and ν and located at points **A** and **B** is therefore another polynomial GTF located at **C** of degree $\mu+\nu$ in x_C, y_C and z_C, which can be expressed as a short expansion of one-centre Gaussians:

$$\chi_{ax}(x)\chi_{bx}(x) = \sum_{i=0}^{\mu+\nu} C_i^{\mu+\nu} \varphi_{ci(x-x_c)} \tag{2.10}$$

where $\varphi_{ci}(x) = x^i e^{-\alpha p(x-x_c)^2}$ and $x_c = \dfrac{\alpha x_a + \beta x_b}{\alpha + \beta}$.

The product of two Gaussians which are functions of the co-ordinates of the same electron is referred to as an *overlap distribution*, and all the integrals which must be calculated involve at least one such overlap distribution. The most important consequence of the GPT is that all four-centre two-electron integrals can be expressed in terms of two-centre quantities. Some properties of the GPT and overlap distributions are explored in Exercise 1.

CRYSTAL actually uses a common and more efficient approach for the evaluation of integrals over Gaussian basis functions[9], in which Hermite Gaussian functions (HGFs) are used instead of the usual Cartesian Gaussians in the re-expansion (2.10). Hermite Gaussians are defined as derivatives of an *s* type Gaussian:

$$\Lambda_i(\xi) = H_i(\xi)\exp\left(-\alpha_p\left(x - x_p\right)^2\right) = (-1)^i \frac{d^i}{d\xi^i}\exp(-\xi^2) \tag{2.11}$$

where $H_i(\xi)$ is a polynomial of order *i*, and

$$\xi = \alpha_p^{\frac{1}{2}}(x - x_p) \tag{2.12}$$

The set of HGFs spans the same space as the expansion functions in (2.10) and as a consequence they can be used for expanding the basis function products:

$$\chi_{ax}(x)\chi_{bx}(x) = \sum_{i=0}^{la+lb} C_i^{la+lb}\Lambda_i(\xi) \tag{2.13}$$

where the expansion coefficients must now be redefined. Because of the natural relations between Hermite polynomials and Gaussians, the necessary two-centre integrals can be evaluated with very high efficiency (see Ref. [10] for a useful discussion). Basis functions with higher quantum numbers can be generated through repeated differentiation of an *s*-type Gaussian.

Even though the four-centre bielectronic integrals can be written in terms of two-centre quantities, the cost of evaluating them still scales nominally as N^4, where N is the number of functions in the expansion. This scaling is far from satisfactory and this must be reduced in order to treat large systems. One way of doing this which is used in CRYSTAL is the method of *pre-screening* where, rather than attempting to calculate the integrals more efficiently, one seeks where possible to avoid their evaluation altogether. Since the expression for an integral over primitive Gaussians can be formally written as

$$\langle ab|cd\rangle = S_{ab}S_{cd}T_{abcd} \tag{2.14}$$

where S_{ab} is a radial overlap between functions χ_a and χ_b , and T_{abcd} is a slowly varying angular factor. In many situations the product S_aS_b thus constitutes a good estimate of the magnitude of the integral, and it may seem attractive to use that product as an estimate in screening out small integrals. In order to estimate these overlaps quickly, a single, normalized *s*-type Gaussian (called an '*adjoined Gaussian*' in the CRYSTAL literature) is associated with each shell, whose exponent α is the smallest of the exponents in the shell contraction. This function thus reproduces approximately the absolute value of the corresponding AOs at intermediate and long range. The adjoined Gaussian is used in fast algorithms for estimating overlaps on the basis of which integrals are either evaluated exactly, approximately, or not at all. The level of approximation is user-definable through a set of tolerances given in the input. Such algorithms, and a consideration of the crystalline symmetry, mean that the CRYSTAL integrals part currently scales at between N and N^2, depending on the size of the system. The most unpleasant scaling in CRYSTAL is thus the SCF part which, since it involves diagonalization of the Fock matrix, scales as approximately N^3.

Plane waves vs. Gaussians

Finally I shall briefly compare the advantages and disadvantage of the simplest alternative to Gaussians in solid-state calculations i.e. plane waves. Plane waves are an orthonormal complete set; any function belonging to the class of continuous normalizable functions (which are those of interest in quantum mechanics) can be expanded with arbitrary precision in such a basis set. The set is universal, in the sense that it does not depend on the positions of the atoms in the unit cell, nor on their nature. We thus do not have to invent a new basis set for every atom in the periodic table nor modify them in different materials as is the case with Gaussian functions, and the basis can be made better (and more expensive) or worse (and cheaper) by varying a single parameter. This characteristic is particularly valuable in *ab initio* molecular dynamics calculations, where nuclear positions are constantly changing. The algorithms mainly (involving fast Fourier transforms) are easier to program since the algebraic manipulation of plane-waves is very simple. It is relatively easy to compute *forces* on atoms, with all the wealth of new physics and chemistry which that implies. Finally, plane-wave calculations do not suffer from *basis set superposition error* (see later). In practice, one must use a finite set of plane waves, and this restricts the detail that can be revealed in real space to such an extent that core electrons cannot be described in this manner. One must either augment the basis set with additional functions (as in e.g. the (F)LAPW scheme), or use pseudopotentials to describe the core states.

In comparison with plane waves, the use of all-electron Gaussian calculations allows us to describe accurately electronic distributions both in the valence and the core region with a limited number of basis functions. The local nature of the basis allows a treatment both of finite systems and of systems with periodic boundary conditions in one, two or three dimensions. This has advantages over plane wave calculations of molecules, polymers or surfaces which work by imposing artificial periodicity: the calculation must be done on e.g. a three-dimensional array of molecules with a sufficiently large distance between them. Gaussian total energies can be made very precise (i.e. reliable to many places of decimals) since all integrals can be done analytically (in practice, this is only true for Hartree-Fock calculations; density functional theory calculations with CRYSTAL require a numerical integration of the exchange-correlation potential which reduces the attainable precision, although this was improved with the release of CRYSTAL98). Having an ‘atomic-like’ basis facilitates population analyses, the computation of properties such as projected densities of states, and ‘pre-SCF alteration of orbital occupation’ (the CRYSTAL

'EIGSHIFT' option)[†]. Many plane-wave programs cannot compute exact non-local exchange which is required not only for Hartree-Fock calculations, but also in the 'hybrid' DFT exchange-correlation functionals and in overcoming self-interaction problems in DFT calculations of Mott insulators[11]. It is now well-understood that localized basis functions are essential for the various new *linear scaling* DFT algorithms that have been the subject of a great deal of recent research[12] and will in all probability be incorporated in a future version of CRYSTAL. The cost that is paid for using Gaussians is the loss of orthogonality, of universality, the need for more sophisticated algorithms for the calculations of the integrals, the difficulty of computing forces (although the next release of CRYSTAL scheduled for early 2001 will include forces for the first time), and an overly heavy reliance on the presence of lots of space group symmetry operators for efficient calculations. As a final note, I have observed that Gaussians are generally more efficient than plane-waves in highly accurate quantum Monte Carlo calculations where symmetry is irrelevant. CRYSTAL may be used to provide initial trial wave functions for the Cambridge QMC code, CASINO[13].

3. Terminology and notation connected with Gaussian basis sets

There is a vast amount of historical quantum chemistry jargon associated with Gaussian basis sets, much of it redundant. Unfortunately it is necessary to understand a certain proportion of it in order to read the literature, but please try to avoid using too much of it yourself.

It has been usual to make a distinction between 'core' basis functions and 'valence' basis functions in Gaussian basis sets. Contractions consisting of primitives with large exponents are associated with the core while more diffuse (small exponent) functions are associated with the valence. This is actually rather arbitrary and is a lingering echo from the past era of Slater orbitals. I stress again that basis functions are not atomic orbitals, and in many cases, they do not even resemble orbitals of isolated atoms. In fact, examining coefficients of true atomic/molecular/crystalline orbitals expanded in such a basis usually reveals that these 'core' basis functions contribute substantially to the highest occupied valence orbitals. This is a consequence of the fact that basis functions on a given center are usually not orthogonal; in addition they are often not really all that compact and overlap to some extent with 'core' functions on neighbouring centers – a situation not likely to occur with true atomic core orbitals.

The early Gaussian contractions were obtained by a least squares fit to Slater orbitals. The number of contractions (not primitives) used for representing a single Slater orbital (i.e. *zeta*) was a measure of the goodness of the set. So, a *single zeta* (or *minimal*) basis set is one that has a single basis function corresponding to each of the atomic orbitals that are occupied in the atom. It is the smallest set one can reasonably use in any calculation, and one should not expect any quantitative accuracy with such a basis. The *double-zeta* basis set consists of two basis functions per atomic orbital, and is thus twice as large as the minimal. In the same way, basis sets of *triple-zeta*, *quadruple-zeta* etc. quality can be built. One often encounters the term *split-valence basis* which basically means a set in which more contractions are used to describe valence orbitals than core orbitals. The letter V denotes split valence sets e.g. DZV

[†] This technique is important, for example, in driving the calculation into particular states in cases like the various transition metal materials where *d* orbital degeneracies are not broken by the crystal field but by high order effects such as spin-orbit coupling e.g. CoO.

represents a basis set with only one contraction for core orbitals and two contractions for valence orbitals. The fact that more basis functions are assigned to valence orbitals does not mean the valence orbitals incorporate more primitives. Usually the core orbitals are long contractions consisting of many primitives to represent well the cusp of the *s*-type function at the nucleus.

One very important and still useful concept is that of *polarization functions*, which are nominally functions of higher angular quantum number than the highest occupied orbital in the system. As an example of why these may be needed, consider an isolated hydrogen atom, the exact wave function of which is just the 1*s* orbital. If the hydrogen atom is placed in a uniform electric field then the charge distribution about the nucleus becomes asymmetric - it is polarized. The lowest order solution to this problem is a mixture of the original 1*s* orbital and a *p*-type function i.e. the solution can be considered to be a hybridized orbital. A hydrogen atom in a molecule experiences a similar, but non-uniform electric field arising from its non-spherical environment. By adding polarization functions i.e. *p*-type functions to a basis set for H we directly accommodate this effect. In a similar way, *d*-type functions which are not occupied in first-row atoms, play the role of polarization functions for the atoms Li to F. Note that the exponents of polarization functions cannot be optimized in atomic SCF calculations and must be reoptimized specifically for the molecule or solid. The 'zeta' terminology is often augmented with a description of the polarization functions. Thus, DZP means double-zeta plus polarization, TZP for triple-zeta plus polarization etc. Sometimes the number of polarization functions is given e.g. TZDP, TZ2P, TZ+2P all stand for triple-zeta plus polarization. The creativity here is evidently extensive.

In molecular work, systems are commonly encountered for which the charge distribution is expected to be considerably more diffuse than in the neutral atom. This is especially true for negatively charged species, or polar systems where a part of the molecule can be expected to carry an excessive negative charge. In this case, it is often advantageous to augment the basis set with *diffuse* functions, i.e. functions that have smaller orbital exponents than those normally used. Diffuse functions are also helpful in calculations when an accurate account of the outer region of the charge density cloud is essential, such as in the calculation of higher-order moments or polarizabilities. It is essential to realize however, that functions involving diffuse primitives are of very little use in the solid state and may even be dangerous, for at least the following three reasons: first the number of integrals to be explicitly calculated increases very quickly as you decrease the exponent; secondly, the accuracy of the calculation must be particularly high in order to avoid pseudo-linear dependence catastrophes (especially when computing exact Fock exchange in HF or hybrid DFT calculations); thirdly diffuse functions are not of much use in densely packed crystals, because their tails are found in regions where there is large variational freedom associated with functions on other atoms.

We have already seen some of the bewildering array of acronyms for the many different kinds of basis sets available. These are essentially just cryptic shorthand for the way the contractions from Gaussian primitives were performed with possibly some description of how the set was modified afterwards. The way in which contractions are derived is not easy to summarize in general, and moreover, it depends upon the intended use for the basis functions. It is a good idea to always read the original paper which describes the contraction procedure. Some basis sets are good for geometry and energies, some are aimed at properties (such as polarizability), some are optimized only with Hartree-Fock in mind, and some are tailored for correlated calculations. Finally, some are good for anions and others for cations and neutral molecules. For some calculations, a good representation of the inner (core) orbitals is necessary (e.g. for properties required to analyze NMR spectra or hyperfine interactions (e.g. ISOTROPIC/ANISOTROPIC keywords in CRYSTAL) or for all-electron Gaussian quantum Monte Carlo calculations), while others require the best possible representation of the valence orbitals.

The most widely-known notation other than the 'zeta' system consists of acronyms like 6-31G. This denotes a basis set where six Gaussian primitives have been used to expand each of the 'core atomic orbitals', whereas the 'valence orbitals' are described by two functions - the inner one expanded in three Gaussians, the outer one uncontracted. It is usual to leave the most diffuse basis functions uncontracted - the outer part of the valence is so strongly distorted from the atomic picture that flexibility is more important than atomic resemblance. To indicate the presence of (any number of) polarization functions an asterisk is added to the basis set symbol. In practice, hydrogen atoms are often treated differently from other atoms in a molecule with regard to the choice of basis set, and polarization functions are not always added to hydrogen atoms. Thus for a set with polarization on all atoms we add two asterisks, 6-31G**. Diffuse functions are treated similarly; a '+' denotes the presence of diffuse functions, '++' denotes that such functions are used on all atoms. A symbol such as e.g. 6-311G**+ would thus be interpreted as follows:

(1) Each atom core orbital is represented by one basis function, expanded in six primitive Gaussians.

(2) Each atom valence orbital is represented by three basis functions, the tightest expanded in three Gaussians, the other two uncontracted.

(3) A set of uncontracted polarization functions has been added on each atom (*p*-orbitals on hydrogen, *d*-orbitals on all other atoms).

(4) A set of diffuse functions (with the same *l*-values as those occurring in the valence orbitals) have been added on all non-hydrogen atoms.

Just for fun before we go any further, let's take a look at the EMSL web library of Gaussian basis set (www.emsl.pnl.gov:2080/forms/basisform.html) used by molecular quantum chemists. I can tell you that the lucky punter is given the choice of the following basis set types (which I am typing in only because I want to concentrate on watching Ally McBeal for half an hour – OK?):

STO-2G, STO-3G, STO-6G, STO-3G*, 3-21G, 3-21++G, 3-21G*, 3-21GSP, 4-31G, 4-22GSP, 6-31G, 6-31G-Blaudeau, 6-31++G, 6-31G*, 6-31G**, 6-31G*-Blaudeau, 6-31+G*, 6-31++G**, 6-31G(3df,3pd), 6-311G, 6-311G*, 6-311G**, 6-311+G*, 6-311++G**, 6-311++G(2d,2p), 6-311G(2df,2pd), 6-311++G(3df,3pd), MINI (Huzinaga), MINI (Scaled), MIDI (Huzinaga), MIDI!, SV (Dunning-Hay), SVP+Diffuse (Dunning-Hay), DZ (Dunning), DZP (Dunning), DZP+Diffuse (Dunning), TZ (Dunning), Chipman DZP+Diffuse, cc-pVDZ, cc-PVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z, pV6Z, pV7Z, cc-pVDZ(seg-opt), cc-pVTZ(seg-opt), cc-PVQZ(seg-opt), cc-pCVDZ, cc-pCVTZ, cc-pCVQZ, cc-pCV5Z, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z, aug-cc-pV6Z, aug-pV7Z, aug-cc-pCVDZ, aug-cc-pCVTZ, aug-cc-pCVQZ, aug-cc-pCV5Z, d-aug-cc-pVDZ, d-aug-cc-pVTZ, d-aug-cc-pVQZ, d-aug-cc-pV5Z, d-aug-cc-pV6Z, Feller Misc. CVDZ, Feller Misc cVTZ, Feller Misc. CVQZ, NASA Ames ANO, Roos Augmented Double Zeta ANO, Roos Augmented Triple Zeta ANO, WTBS, GAMESS VTZ, GAMESS PVTZ, Partridge Uncontr. 1, Partridge Uncontr. 2, Partridge Uncontr. 3, Ahlrichs VDZ, Ahlrichs, pVDZ, Ahlrichs VTZ, Ahlrichs TZV, Binning/Curtiss SV, Binning/Curtiss VTZ, Binning/Curtiss SVP, Binning-Curtiss VTZP, Mclean/Chandler VTZ, SV+Rydberg

(Dunning-Hay), SVP+Rudberg (Dunning-Hay), SVP+Diffuse+Rydberg, DZ+Rydberg (Dunning), DZP+Rydberg (Dunning), DZ+Double Rydberg (Dunning-Hay), SV+Double Rydberg (Dunning-Hay), Wachters+f, Bauschlicher ANO, Sadlej pVTZ, Hay-Wadt MB(n+1)ECP, Hay-Wadt VDZ(n+1)ECP, LANL2DZ ECP, SBKJC VDZ ECP, CRENBL ECP, CRENBS ECP, Stuttgart RLC ECP, Stuttgart RSC ECP, DZVP (DFT Orbital), DZVP2 (DFT Orbital), TZP (DFT Orbital), DeMon Coulomb Fitting, DGauss A1 DFT Coulomb Fitting, DGauss A1 DFT Exchange Fitting, DGauss A2 DFT Coulomb Fitting, DGauss A2 DFT Exchange Fitting, Ahlrichs Coulomb Fitting, cc-pVDZ-fit2-1, cc-pVTZ-fit2-1, cc-pVDZ_DK, cc-pVTZ_DK, cc-pVQZ_DK, cc-pV5Z_DK, cc-pVDZ(pt/sf/fw), cc-PVTZ(pt/sf/fw), cc-pVQZ(pt/sf/fw), cc-pV5Z(pt/sf/fw), cc-pVDZ(fi/sf/fw), cc-pVTZ(fi/sf/fw), cc-pVQZ(fi/sf/fw), cc-pV5Z(fi/sf/fw), cc-pVDZ(pt/sf/sc), cc-pVDZ(pt/sf/lc), cc-pVTZ(pt/sf/sc), cc-PVTZ(pt/sf/lc), ccp-PVQZ(pt/sf/sc), cc-pVQZ(pt/sf/lc), cc-PV5Z(pt/sf/sc), cc-PV5Z(pt/sf/lc), cc-pVDZ(fi/sf/sc), cc-PVDZ(fi/sf/lc), cc-PVTZ(fi/sf/sc), cc-PVTZ(fi/sf/lc), cc-PVQZ(fi/sf/sc), cc-PVQZ(fi/sf/lc), cc-PV5Z(fi/sf/sc), cc-pV5Z(fi/sf/lc), Pople-Style Diffuse, STO-3G* Polarization, 3-21G* Polarization, 6-31G* Polarization, 6-31G** Polarization, 6-311G* Polarization, 6-311G** Polarization, Pople (2d/2p) Polarization, Pople (3df,3pd) Polarization), HONDO7 Polarization, Huzinaga Polarization, Dunning-Hay Diffuse, aug-cc-pVDZ Diffuse, aug-cc-pVTZ Diffuse, aug-cc-pVQZ Diffuse, aug-cc-pV5Z Diffuse, aug-cc-pV6Z Diffuse, aug-pV7Z Diffuse, d-aug-cc-pVDZ Diffuse, d-aug-cc-pVTZ Diffuse, d-aug-cc-pVQZ Diffuse, d-aug-cc-pV5Z Diffuse, d-aug-cc-pV6Z Diffuse, DHMS Polarization, Dunning-Hay Rydberg, Dunning-Hay Double Rydberg, Binning-Curtiss (1d Polarization), Binning-Curtiss (df) Polarization, Ahlrichs Polarization, Glendenning Polarization, Blaudeau Polarization, Core/val. Functions (cc-pCVDZ), Core/val. Functions (cc-pCVTZ), Core/val. Functions (cc-pCVQZ), Core/val. Functions (cc-pCV5Z).

I hope you can see that this would become an increasingly unprofitable exercise if I commented further. Let me conclude this section by stating how I think CRYSTAL users might record their basis sets in published work. First of all (and I'm generalizing only a little) it is a sad fact that true molecular quantum chemists will not believe any work you do unless it is done with a 'named and published' basis set with the name in question being one of the ten or so people in the above list. This is a cross we all have to bear. Kill yourself or get over it. In my opinion, the simplest and most sensible notation for CRYSTAL users who develop their own sets might be something like "In this piece of terrifically important research we used a basis of contracted Gaussian-type functions of the form $s(9)sp(7)sp(6)sp(3)sp(1)d(4)d(1)$ for element A and $s(8)sp(6)sp(3)sp(1)$ for element B, where the letters give the shell type and the numbers in brackets give the number of primitive Gaussians in each shell contraction. The exponents and contraction coefficients are reported in appendix X/TableY/Web Site Z." This conveys all relevant information, there is no need to decide on some semi-arbitrary core-valence partition and, being familiar with the periodic table, the reader is able to work out for herself whether the set includes polarization functions or not. And for God's sake don't invent any more acronyms.

Basis sets in CRYSTAL

The basis set information in the CRYSTAL input deck is reasonably straightforward, and may be understood through the example given on the following page:

```
28 7                 nickel basis with seven shells
0  0  8  2.0  1.0
      367916.0      0.000227
       52493.9      0.001929              basis set type for this shell:
       11175.8      0.0111                0 = general basis set, given as input (like this)
        2925.4      0.05                  1 = STO-nG (Z=1-54)
         882.875    0.1703                2 = Pople 3(6)-21G (Z = 1-54(18))
         305.538    0.369
         119.551    0.4035                shell type (0 = s, 1 = sp, 2 = p, 3 = d)
          49.9247   0.1426
0  1  6  8.0  1.0
         924.525   -0.0052    0.0086      number of primitive Gaussians in this shell
         223.044   -0.0679    0.0609
          74.4211  -0.1319    0.2135      scale factor
          29.6211   0.2576    0.3944     NB:[(scale factor)^2 × exponent in contraction]=true exponent
          12.4721   0.6357    0.3973      formal electronic charge attributed to the shell
           4.2461   0.2838    0.2586
0  1  4  8.0  1.0
          56.6581  -0.0124   -0.018       exponent of normalized primitive Gaussian
          21.2063  -0.2218   -0.08
           8.4914  -0.8713    0.2089      s contraction coefficient
           3.6152   1.0285    1.255   ←   p contraction coefficient
0  1  1  0.0  1.0
           1.5145   1.0       1.0
0  1  1  0.0  1.0
           0.6144   1.0       1.0
0  3  4  8.0  1.0
          41.08     0.040500
          11.4126   0.202200
           3.856    0.433800
           1.33     0.489700
0  3  1  0.0  1.0
           0.411    1.0
8 4                oxygen basis with four shells
0  0  8  2.0  1.0
        8020.0      0.00108
        1338.0      0.00804
         255.4      0.05324
          69.22     0.1681
          23.90     0.3581
           9.264    0.3855
           3.851    0.1468
           1.212    0.0728
0  1  4  8.0  1.0
          49.43    -0.00883   0.00958
          10.47    -0.0915    0.0696
           3.235   -0.0402    0.2065
           1.217    0.379     0.347
0  1  1  0.0  1.0
           0.4764   1.0       1.0
0  1  1  0.0  1.0
           0.1802   1.0       1.0
99 0               end of basis set input
```

All-electron basis set for nickel oxide (NiO)

Two sets of all electron basis sets are included as internal data in the CRYSTAL code, neither of which are worth using any more. Nevertheless, they are:

(1) *the minimal STO-nG basis sets of Pople and co-workers (atomic nos. 1-54)*

These basis sets are designed to mimic the shape of Slater-type functions, and are obtained by fitting STOs with *n* contracted primitive Gaussians (where *n* is generally between 2 and 6). Such a fit can be done accurately and the main limitation to the usefulness of these sets appears to be that the STO itself is not a perfect basis function. They are still used occasionally in spite of the poor quality of the resulting wave function, presumably because they are well-documented and generally provide, due to fortuitous cancellation of errors, reasonable optimized geometries at low cost.

(b) *split-valence 3-21 and 6-21 basis sets*

In these sets, the core shells are described as a linear combination of three (up to atomic number 54) or six (up to atomic number 18) Gaussian primitives with the two valence shells containing two and one Gaussians. The exponents and contraction coefficients have been variationally optimized for the isolated atoms, and *s* and *p* functions of the same shell share the same exponent. A single set of polarization functions (*p*, *d*) can be added without causing numerical problems. Standard molecular polarization functions are usually also adequate for periodic compounds.

4. Basis set selection

In choosing a basis set the paramount but conflicting issues are accuracy and computational cost. These are obviously inversely related, and there is little more to be said about it. However, computational cost alone should not determine what basis set is used. Selecting a smaller set purely on the basis of a lack of sufficiently powerful computers or interest will often prove unsuitable for describing the system in question, which rather defeats the object of performing the calculation in the first place. The minimum basis set requirements of all properties to be computed should always be considered.

A great deal of general experience has now been gained by computational chemists in selecting appropriate basis sets for molecular problems[14], and much of this experience can be used in the selection of basis sets for studies of crystalline solids. However, I think it is true to say that the molecular quantum chemists do not in general like to *optimize* basis sets by varying the exponents or contraction coefficients to minimize the energy (and this is not necessarily their fault since the most popular codes such as GAUSSIAN do not include a facility for doing so, other than by laborious hand optimization). Rather, as we have seen, there is a *hierarchy* of basis sets with perceived qualities, and for a difficult problem where accuracy is important one would use a ‘good quality’ standard basis set from a library without modification. The literature is full of statements like ‘this calculation was carried out at the STO-2G level’ (probable translation: this calculation is rubbish, but my molecule is just *too* big) or ‘this property was calculated at the TZVP level’ (i.e. it’s probably quite good). In crystalline systems by contrast, basis set optimization is usually necessary, essentially for two reasons. Firstly, there is a much larger variety of binding than in molecules and basis sets are thus less transferable. For example, carbon atoms may be involved in strong covalent bonds, e.g. in polyacetylene or diamond, as well as in highly ionic systems such as Be_2C, where the Mulliken charge of carbon is close to –4. Secondly, hierarchical libraries of basis sets comparable to those available for molecules do not really exist. For certain types of compound, such as molecular crystals (e.g. urea) or many covalent materials, the molecular sets can sometimes be used largely unmodified (although I don't necessarily recommend it). However, for strongly ionic crystals and metals the basis sets, particularly the valence states, need to be redefined completely. In essentially all cases, the core states may be described using the solutions of atomic calculations, as even in the presence of strong crystal fields the core states are barely perturbed and may be described by the linear variational parameters in the SCF calculation.

Redefining basis sets in this way is obviously time consuming and even more obviously rather boring, and so over the last five years various people involved with the CRYSTAL program have contributed to an effort to develop libraries of basis sets for CRYSTAL to be made available on the internet. The URL of the official site is:

www.ch.unito.it/ifm/teorica/crystal/AEbasisset/mendel.html

The site shows a periodic table. Clicking on the symbol for the required element will reveal a text file containing various different basis sets which may have been used in different materials containing that element type. Accompanying each basis set is list of authors, a list of materials where the set has been used, references to publications and hints on optimization where relevant. This table, which is obviously not complete, grew out of a set of text files compiled largely by me whilst working in Torino in 1995. Since my departure to Cambridge in early 1997, I have maintained my own separate library whose content has now diverged significantly from that of the official site. It is a little more 'experimental' in the sense that it contains sets which have never been used in published calculations, and also sets which have simply been optimized in atomic SCF calculations but then never developed further. The aim of providing such untried sets is to starting points for reoptimization where one hopes that at least the core functions are reasonable. In particular it contains almost all of the heavier elements beyond zinc in the periodic table up to around lanthanum where we are forced to stop because of the lack of *f* functions in CRYSTAL. The URL of the Cambridge library is:

www.tcm.phy.cam.ac.uk/~mdt26/crystal.html

There is a link from this page to the Cambridge quantum Monte Carlo page, which will shortly include a table of basis sets found to have been useful in QMC calculations. Finally, if you want to obtain standard molecular basis sets to use as starting points for solid calculations (or even to do molecular calculations), you can find the very useful EMSL library at:

www.emsl.pnl.gov:2080/forms/basisform.html

For European users, this serviced is mirrored at Daresbury Laboratory at:

wserv1.dl.ac.uk:800/emsl-pnl/basisform.html

Presently I shall discuss reoptimization strategies for the basis sets given in the standard CRYSTAL libraries and also discuss the adaptation of molecular bases for various types of solid. First of all a number of general principles are given that should be taken into account when choosing a basis set for a periodic problem.

a. Diffuse functions

The pre-screening procedure used in CRYSTAL is based on overlaps between Gaussian *s* functions associated with each shell whose exponents are set equal to the lowest exponent of all the primitive Gaussians in the contraction. The number of integrals to be calculated thus increases very rapidly with decreasing exponents of the primitive Gaussians, an effect which is much less pronounced in molecular calculations. The following table shows that the cost of HF calculations on silicon and diamond, which for such small systems is determined almost exclusively by the number of bielectronic integrals, can increase by a factor of 10 simply by changing the exponent of the most diffuse single Gaussian from 0.168 to 0.078 (Si) and from 0.296 to 0.176 (C). The cost is largely dominated by this shell, despite the fact that large contractions are used for the 1*s*, 2*sp* and the innermost valence shell. The last entries in the table are examples of weird behaviour - see part *c*.

	Diamond			**Silicon**	
α	N	E_{HF}	α	N	E_{HF}
0.296	58	–75.6633	0.168	46	–577.8099
0.276	74	–75.6728	0.153	53	–577.8181
0.256	83	–75.6779	0.138	72	–577.8231
0.236	109	–75.6800	0.123	104	–577.8268
0.216	148	–75.6802	0.108	151	–577.8276
0.196	241	–75.6783	0.093	250	–577.8266
0.176	349	no convergence	0.078	462	no convergence

Table 4.1 - Total Hartree-Fock energy E_{HF} per cell and number of bielectronic integrals in 10^6 units (N) to be evaluated as a function of the exponent (α) of the outer shell for diamond and silicon. In both cases a 'split-valence' 6-21G basis set was used. You can repeat the silicon calculations with 'test10' in the CRYSTAL98 distribution if you want.

In atoms and molecules a large part of the additional variational freedom provided by diffuse functions is used to describe the tails of the wave function, which are poorly described by the long-range decay of the Gaussian function. In crystalline compounds by contrast, particular in non-metallic systems, the large overlap between neighbours in all directions drastically reduces the contribution of low-exponent Gaussians to the wave function. This has the consequence that a small 'split-valence' basis set such as 6-21G is closer to the Hartree-Fock limit in crystals than in molecules.

b. Number of primitives

As discussed previously, a typical basis set will have 'core functions' with higher exponents and a relatively large number of primitives - these will have a large weight in the expansion of the core states. The 'valence functions' with a large weight in the outer orbitals will have lower exponents and contractions of only a very few primitives. We can get away with putting a lot of primitives in the core since core states have very little overlap with neighbouring atoms and thus the use of a large number of primitives in the GTF contraction is of limited cost in CPU time. The use of many primitives in the valence shells would add significantly to the cost of a calculation.

c. *Numerical catastrophes*

Under certain conditions a CRYSTAL calculation may fall into a non-physical state during the SCF part characterized by an oscillating total energy significantly higher than the true energy. Such calculations will not, in general, converge. It is observed that the risks of numerical problems like this increases rapidly with decreasing value of the most diffuse Gaussian exponent in the basis set. It happens, for example, in the silicon calculation reported in Table 4.1 where the exponent of the most diffuse basis function is 0.073. In general this behaviour may be attributed to limitations in the accuracy of the Coulomb and exchange series evaluation. The exchange is by far the more delicate of the two series since long-range contributions are not taken into account and because the 'pseudoverlap' criteria associated with the two overlap parameters ITOL4 and ITOL5 mimic the real behaviour of the density matrix only in an approximate way. This means that calculations which require exact Fock exchange (i.e. Hartree-Fock, hybrid DFT) are at much greater risk of showing this behaviour. An LDA-DFT calculation of our errant Si calculation actually works perfectly well.

In order to obtain physical solutions in situations like this, the usual remedy is to increase the integral tolerances to give higher precision via the TOLINTEG keyword. For non-metallic systems with medium-sized basis sets, the default integral tolerances of 6 6 6 6 12 are adequate for the optimization of the exponents of the valence shell and for systematic studies of the energy versus volume curves. However, in metals, the optimization of the energy versus exponent curve at the Hartree-Fock level is often not even possible, even with much higher integral tolerances. If you insist on studying metals with HF, reasonable values of the valence shell exponent (say 0.23 for beryllium and 0.10 for lithium) can be used for the study of the structural and electronic properties of metallic systems even though they don't correspond to a variational minimum. Use DFT instead.

d. *Basis set superposition error*

A rather serious problem associated with Gaussian basis sets is *basis set superposition error* (BSSE). A common response to this problem is to ignore it, since it will go away in the limit of a complete basis. Sometimes this approach is justified, but this requires investigation that is seldom performed, and some understanding of BSSE is indispensable in order to perform accurate and reliable calculations. The problem of BSSE is a simple one: in a system comprising interacting fragments A and B, the fact that in practice the basis sets on A and B are incomplete means that the fragment energy of A will necessarily be improved by the basis functions on B, irrespective of whether there is any genuine binding interaction in the compound system or not. The improvement in the fragment energies will lower the energy of the combined system giving a spurious increase in the binding energy. It is often stated that BSSE is an effect that one needs to worry about only in calculations on very weakly interacting systems. This is not really true. BSSE is an ever-present phenomenon and accurate calculations should always include an investigation of BSSE. Examples of areas in which one should be particularly wary are the study of the binding energy of molecules adsorbed on surfaces (see, for example Ref [15] for an interesting discussion) or the calculation of defect formation energies..

The approach most commonly taken to estimate the effect of BSSE is the *counterpoise correction*[16]: the separated fragment energies are computed not in the individual fragment basis sets, but in the total basis set for the system including 'ghost functions' for the fragment that is not present. These energies are then used to define a counterpoise-corrected (CPC) interaction energy, which by comparison with perturbation theory, has been shown to converge to the BSSE-free correct value[17]. An example of how to compute the counterpoise correction using CRYSTAL in a calculation on a simple model system (CO adsorbed on MgO (100) surface) affected by BSSE will be given in Exercise 2.

e. *Pseudopotentials*

It is well known that core states are not in general affected by changes in chemical bonding. The idea behind pseudopotentials is therefore to treat the core electrons as effective averaged potentials rather than actual particles. Pseudopotential are thus not orbitals but modifications to the Hamiltonian and are used because they can introduce significant computational efficiencies. In plane wave calculations, pseudopotentials are essentially mandatory since the core orbitals have very sharp features in the region close to the nucleus and too many plane waves would be required to expand them if they were included. The most important characteristic of a pseudo designed for such calculations is that it is as smooth as possible in the core region. Pseudopotentials in Gaussian basis set calculations are not mandatory and have different characteristics to those designed for plane waves since Gaussians actually have sharp features in the core region. If the CPU time in CRYSTAL is dominated by the integrals calculation, they will not even buy you very much since the number of integrals is controlled by more diffuse functions which overlap strongly with neighbouring atoms – something which basis functions with large weight in the core orbitals are not very good at. However the use of pseudopotentials will decrease the number of coefficients in the wave function and might give significant savings in the SCF part. It is also quite easy to incorporate *relativistic effects* into pseudopotentials which is increasingly important for heavy atoms. All electron relativistic calculations are very expensive and not possible in CRYSTAL anyway. Some people have used pseudopotentials to overcome the problem of the missing *f* Gaussian basis functions in CRYSTAL and have done calculations on heavy atoms containing *f* electrons. How does the use of pseudopotentials modify the basis set in Gaussian calculations? Take an all-electron basis set for that atom. First of all one might hope that basis functions which have a large weight only in the core orbitals might be removed. Remove them. Make sure you are left with the correct number of electrons. The remaining basis functions must then be optimized (see later) with reference to the pseudopotential.

5. Practical optimization

So to summarize, there are a number of approaches to developing a basis set for a periodic HF/DFT calculation. Obviously the easiest way is to download standard sets from the online libraries or ask experienced CRYSTAL users and to use these sets without modification. The second way is to start from one of these standard sets and improve it. The third way is to suitably modify a molecular basis set for use in your crystalline system. The fourth way is to develop a basis set from scratch using atomic SCF calculations, probably using a nearby atom in the periodic table as a starting point. Let us summarize first of all some ways 'one might' improve a basis set:

- *Reoptimize* the more diffuse exponents (and contraction coefficients if necessary).
- *Decontract* i.e. convert the more diffuse contractions into single Gaussian primitives.

- *Convert sp functions* into separate *s* and *p* functions.
- *Add polarization functions* if not already present
- *Add more primitives* (watch out for linear dependence problems).
- *Use a better starting point*

Reoptimization in this sense means varying an appropriate subset of the basis set parameters until the energy is minimized. In principle this is a reasonably complex multidimensional minimization, but there are various standard shell scripts available to help you with this (see later). Be careful that the ratio between succesive exponents doesn't fall below 2-2.5, otherwise the basis may suffer from linear dependence problems. Watch the CPU time, particularly when carrying out decontraction, or adding polarization functions.

By means of some (very simple) examples I will now briefly consider the adequacy of molecular basis sets for different types of crystalline compound. Note that the basis sets discussed are hardly 'state of the art' and are meant to illustrate particular principles only. Note also that I have 'adapted' some of these discussions from those given in the CRYSTAL manual.

Covalent systems

Let's consider again two (stereo)typically covalent systems, diamond and silicon. I will use the CRYSTAL standard 'split-valence' 6-21G basis sets, that is, the core shells are described with a contraction of six primitive Gaussians and the inner and outer valence shells contain respectively two and one Gaussians. *sp* shells are used throughout, in that the *s* and *p* functions of the same shell share the same exponent, and all contraction coefficients are variationally optimized in the isolated atoms. The best exponent of the outer shell of the atom is 0.196 for C and 0.093 for Si. Reoptimization of the valence shell of C in two molecules gave 0.24 in CH_4 and 0.189 in CO for these quantities[18]. Repeating the optimization in the two crystalline compounds reveals that the most internal valence shell is essentially unaltered with respect to the atomic solution, while for the outer single-Gaussian shell the best exponent is 0.22 for diamond and 0.11 for silicon. These values are very similar to those optimized in the isolated atoms. If a single-Gaussian *d* polarization shell (which is five separate functions) is added to the 6-21G basis (i.e. to give 6-21G*) and the exponents optimized one gets 0.8 for diamond and 0.4 for silicon. These values are very close to those resulting from the molecular optimization, which are 0.8 for diamond[19] and 0.45 for silicon[20]. It seems therefore that small molecular split-valence basis sets can therefore be used with confidence and essentially without modification to describe covalent crystals. It is generally advisable however to reoptimize the exponent of the most diffuse shell, which produces a slightly improved basis, while reducing the cost of the calculation. That said, 6-21G* is not really all that good and a larger better basis set with more variational freedom is quite easy to make for these cases (see web libraries).

Ionic crystals

The classification of materials as covalent or ionic is a conventional one but the division between the two is necessarily rather blurred. Examples of more or less *fully ionic* compounds are LiH and MgO, and for these systems the cation valence shell is almost completely empty. For such cations it often proves convenient to use a basis set containing only 'core' functions plus an additional *sp* shell with a relatively high exponent. As an example, in previous work using CRYSTAL such *sp* shells were used for Mg in MgO and for Li in LiH, Li_2O and Li_3N with respective exponents of 0.3-0.4 and 0.5-0.6 [21]. Total energies obtained either by using only core functions for Li/Mg or by adding a 'valence' shell to the cation differed by less than 0.1eV/atom. This figure was essentially the same for a relatively large range of exponents of the outer shell, say 0.2-0.5 for Mg. It is usually difficult, and often impossible, to optimize the exponents of functions which only have appreciable weight in almost empty orbitals; one finds that the energy decreases almost linearly with the exponent. As discussed in the previous section, very low exponent values require the calculation of enormous numbers of integrals and may lead to numerical instabilities. Thus for ionic crystals with nearly empty shells, and where the energy gain of optimization is relatively small (say, a decrease in energy of less than 1 mHartree for a change in α of around 0.2) it is usually convenient to use a relatively large exponent for this shell.

Anions present a different problem. Reference to isolated ion solutions is possible only for halides, because in such cases the ions are stable even at the Hartree-Fock level. For other anions, which are stabilized by the crystalline field (such as H^-, O^{2-}, N^{3-} and C^{4-}), the basis set must be redesigned with reference to the crystalline environment. Consider, for example, the optimization of the O^{2-} basis set in Li_2O. The difficulty is to allow the valence distribution to relax in the presence of two more electrons. We begin from a standard STO-6G basis set i.e. six contracted primitive Gaussians for the 1*s* shell, and six more to describe the 2*sp* shell. First of all, two more Gaussians were introduced into the 1*s* contraction, in order to improve the virial coefficient and total energy. The two outer Gaussians of the valence *sp* shell were then removed from the contraction and allowed to vary independently. The exponents of the two outer independent Gaussians and the coefficients of the four contracted ones were optimized in Li_2O. The best outer exponents of the *ion* were found to be 0.45 and 0.15 and are therefore considerably more diffuse than the *neutral* isolated atom, where the best exponents are 0.54 and 0.24. The rest of the O^{2-} valence shell is unchanged with respect to the atomic situation. The introduction of *d* functions in the oxygen basis set gives only a minor improvement in the energy of 1×10^{-4} Hartree per cell, with a population of 0.02 electrons/atom/cell (*d* functions may be important in the calculation of certain properties however - see later). Thus for anions, reoptimization of the most diffuse valence shells is mandatory when starting from a standard basis set.

Semi-ionic crystals

Intermediate situations should be considered individually and the adequacy of selected basis sets must be carefully tested. Examples of semi-ionic compounds are α-quartz (SiO_2) and corundum (Al_2O_3). The exponents of the outer shell for the two cations in the 6-21G basis are 0.093 (Si) and 0.064 (Al). In both cases, this function proves to be too diffuse, even causing numerical catastrophes at the HF level in the Al case. For quartz, reoptimization in the bulk gives α=0.15 for Si (the dependence of the total energy on α is much smaller than in pure silicon (Table 4.1) and the cost at α=0.15 is only 50% of the one at α=0.09). In contrast the best molecular and crystalline exponent for oxygen (α=0.37) coincide. Corundum is more ionic than quartz, and about two valence electrons are transferred to oxygen. In this case it is better to eliminate the most diffuse valence shell of Al, and to use as independent functions two Gaussians of the inner valence shells (α=0.94 and 0.3 respectively).

Metals

It is often stated[22] that Gaussian basis sets are somehow inappropriate for describing simple metals and that plane-waves, for example, are a more ‘natural’ basis via some sort of analogy with the orbitals of the free electron gas (which *are* plane-waves). However until recently very few studies had been done to argue properly one way or the other. The reason for this has its origin in the fact that to reproduce the nearly uniform density characterizing simple metallic systems such as lithium and beryllium one needs to use very diffuse Gaussians. You will recall from an earlier section that this is a very bad idea in Hartree-Fock because of the Fock exchange pathology and it is generally impossible to optimize the basis set in such cases. Until DFT calculations became possible (with the 1995-1996 release of CRYSTAL) it was thus quite difficult to separate the effects of basis set and Hamiltonian. The few Gaussian DFT studies that have been done since then seem to indicate that GTFs are able to provide a reliable and efficient description of simple metallic systems[23,24].

An interesting example of a CRYSTAL study of a metallic system is that of Doll, Harrison and Saunders[24] who investigated the effect of computational parameters (including the basis set) on the calculated surface and bulk properties of metallic lithium. This system will be used in Exercise 3, and therefore a certain amount of apparently irrelevant detail will be presented here. Doll *et al.* began with the following core *s* function taken from an earlier study[25]:

```
0 0 6 2.0 1.0
840.0  0.00264
217.5  0.00850
72.3   0.00335
19.66  0.1824
5.44   0.6379
1.5    1.0
```

Keeping this core function fixed, they then proceeded to add functions to this basis of increasing complexity and examined the convergence of various properties:

- BASIS SET 1 [*s*(6)*sp*(1)*sp*(1)]: The *sp* exponents were optimized with LDA (or PWGGA) to 0.5 and 0.08. However, as an exponent of 0.08 gives rise to a diffuse basis function close to numerical instability and was quite expensive, exponents of 0.5 and 0.1 were in fact used.
- BASIS SET 2 [*s*(6)*sp*(1)*sp*(1)*sp*(1)]: ‘even tempered’ exponents (i.e. the ratio between the exponents is kept fixed - to 2.5 in this case). Exponents 0.5, 0.2, 0.08. This ratio is close to the lowest which can be tolerated before on-site (atomic) linear dependence is seen. It is however also known from previous work to converge the atomic energy to within less than 0.0001 Ha of the exact Hartree-Fock ground state energy.
- BASIS SET 3: [*s*(6)*sp*(1)*sp*(1)*sp*(1)*d*(1)] Just like BASIS SET 2 but with a *d* polarization function, whose exponent was optimized with a PWGGA functional to be 0.15. However, the *d* function leads only to a minor change in the total energy. Changing the exponent to 0.5 changes the energy only by around 0.00005 Ha.

As expected from previous discussions about the Fock exchange pathology, an optimization of the basis set exponents was not possible either at the Hartree-Fock level or using the B3LYP hybrid DFT functional: the outermost exponent became more and more diffuse until finally the solution became unstable.

One of the properties computed by Doll *et al.* was the cohesive energy for which accurate energies of the free atom are also required. A richer basis set is required to compute this accurately because of the need to describe the long-range behaviour of the atomic wave function (note the absence of p functions):

- BASIS SET 4: [$s(6)s(1)s(1)s(1)s(1)s(1)$] with outer exponents of 0.6, 0.24, 0.0096, 0.04 and 0.0016.

In the LDA and PWGGA calculations it is also required to expand the exchange and correlation potentials in an *auxiliary basis set*. Doll *et al.* went beyond the defaults and used a set consisting of 13 even-tempered s-functions with exponents from 0.1 to 2000, 3 even-tempered p-functions with exponents from 0.1 to 0.8, and 2 d-functions with exponents of 0.12 and 0.3. This is sufficient to integrate the charge density to an accuracy of 10^{-7} $|e|$. For the free atom, they used an auxiliary basis set with 18 even-tempered s-functions with exponents from 0.0037 to 4565.

In metals the reciprocal space sampling is also a critical and rather delicate issue. In CRYSTAL the sampling is performed on a Monkhorst-Pack net where the density of points is determined by a shrinking factor. The Fermi energy and shape of the Fermi surface are determined by interpolation onto a 'Gilat' net. This net is simply related to the Monkhorst-Pack net by an additional subdivision factor. To further improve convergence, the finite temperature generalization of density functional theory can be used to apply Fermi surface smearing (with the SMEAR keyword). Note that a higher number of sampling points in the Gilat net leads to a systematic improvement at zero temperature. At finite temperature, the number of Gilat points does not influence the results so long as the MP net is sufficiently dense. Properties were investigated using smearing of 0.001Ha and 0.02 Ha. It was found that a shrinking factor of 16 for the MP net and a temperature of 0.001Ha gave good results (i.e. convergence of the energy to at least 0.0001 Ha with respect to reciprocal space sampling.

The conclusions of Doll *et al.* were essentially as follows. The cohesive energy and lattice constant were stable even with the smallest of the basis sets. The elastic constants and surface energies were more sensitive to basis set. The converged values of all properties were in full agreement with experiment and calculated values from the literature. The results in best agreement with experiment were obtained with the Perdew-Wang GGA funtional. Hartree-Fock and hybrid functionals were very difficult because of the Fock exchange pathology. Finite temperature calculations could be used to improve convergence and an extrapolation to zero temperature was both possible and accurate. [Now why not try Exercise 3?].

Transition elements

A particularly interesting new field to which CRYSTAL has been applied over the last six or seven years is that of magnetic compounds containing transition elements. These are examples of what physicists refer to as 'strongly correlated materials'. Such materials have been the subject of controversy due to the great difficulties that density functional theory calculations (based on LDA or GGA functionals) have had in this area, with magnetic insulators being predicted to be metals and so on. Lest previous sections of these notes have convinced you that Hartree-Fock calculations are actually rather useless, it turns out that UHF actually gets the ground state qualitatively correct in magnetic insulators (I will briefly explain this shortly). A collaboration between the Torino and Daresbury (and other) groups beginning in 1993 was able to demonstrate this and helped to highlight the problem with DFT. Relevant papers from that time can be found in References[26,27,28,29,30,31,32,33] and since then a great deal of other work has been done by a wide variety of groups [34]. A talk attempting to explain this topic in simple terms for first-year graduate students is available on the web at www.tcm.phy.cam.ac.uk/~mdt26/tmo/scm_talk.html.

So, what is a strongly correlated material? 'Strongly-correlated' is a term used in many-body physics to mean that a particular parameter in a 'toy' model (referring to 'on-site' intratomic Coulomb interactions) is bigger than other parameters in the model (related to the band width, or kinetic energy). It should not be confused with 'correlation' in the quantum chemistry sense, which is the energy difference between the exact non-relativistic energy and the Hartree-Fock energy in the limit of a complete basis set. What characteristics of a material, from the point of view of its electronic structure, make it strongly correlated? This is a good question. To begin with, it is generally assumed that electrons in strongly-correlated materials are 'localized' in some sense (see Professor Resta's talk for a definition of this) and their constituent atoms retain much of their free-atom-like characteristics. It is thus convenient to consider such problems in real, as opposed to reciprocal space. To a first approximation you might think of the crystalline orbitals corresponding to the $3d$ states in such materials as periodic arrays of particular atomic d orbitals (such as the d_{xz} or d_{yz} or whatever) multiplied by a phase factor with some $\mathbf{k}$. As a function of $\mathbf{k}$ these will form relatively narrow bands. To create an insulating state, some of these bands must be full and some must be empty. What mechanism exists for splitting the sub-bands within the d manifold?

- *Crystal field splitting*: in the presence of a cubic crystal field (for example) due to the presence of neighbouring atoms the d manifold will be split into e_g (d_{x2-y2} and d_{z2}) and t_{2g} (d_{xy},d_{xz},d_{yz}) subsets. The energy scale of this is often rather small.
- *Exchange splitting*: Electrons of the same spin tend to stay out of each other's way because of the exchange interaction, and so the interelectronic Coulomb repulsion will be smaller for the majority-spin electrons The majority-spin bands will therefore be lowered in energy with respect to the minority spin bands (this can split up-spin e_g bands and down-spin e_g bands for example).

But what mechanism exists for splitting the subbands corresponding to the two different e_g orbitals of the same spin?

- *On-site Coulomb interactions*: we populate one of the e_g orbitals with an up-spin electron and leave the other empty. Imagine there are n electrons on this particular transition metal ion. Thus an electron in the occupied e_g sub-band feels the potential of $n-1$ electrons and an 'added' electron in the virtual orbital would feel the potential of n electrons. The difference is the on-site Coulomb interaction U (which is the 'strong correlation' i.e. a sort of screened intra-atomic Hartree interaction).

It turns out that such behaviour can be replicated at the UHF level with a single determinant wave function. The reason for the failure of LDA/GGA calculations to do the same is interesting. Within the LDA, the potential felt by each electron is computed from a functional of the total electron densities. For such simple density functionals this leads to eigenvalues which are relatively weak functions of the particular orbital occupancy. Ultimately this behaviour stems from the spurious inclusion of 'self-interaction’ effects in the exchange-correlation potential (the interelectron Coulomb energy in a one-electron atom is non-zero using the LDA!). In HF theory, the non-local exchange exactly cancels the self-interaction and introduces a strongly orbitally-dependent potential which splits the manifold of *d* states in precisely the manner expected from a simple empirical (‘Hubbard model’) estimate of the on-site interactions between electrons in different orbitals. Indeed a variety of new ‘DFT’ schemes (e.g. LDA+U, SIC-LDA) which emulate important features of the Hartree-Fock Hamiltonian have now been developed which give better descriptions of the on-site interactions than regular DFT. New 'exact-exchange' DFT formulations are currently the focus of intense research and also hold a great deal of promise. So the point is that although DFT is in principle exact and you can compute the total energy as a functional of the density, the eigenvalue spectrum does not necessarily correspond to anything physical (since the orbitals are merely auxiliary functions used to parameterize the density). Unfortunately having the wrong eigenvalue spectrum means that KS-DFT calculations will sometimes converge to an incorrect ground state with the wrong density.

To treat systems like these with any degree of accuracy at the UHF level in CRYSTAL (or at the hybrid DFT level which is also promising) reasonably good basis sets for the transition elements are required. These are not that widely available even to molecular quantum chemists since until relatively recently most of the effort in developing molecular GTF basis sets has been for first- and second-row atoms. One reason for this may be that *molecules* containing transition metal atoms tend to be very badly described at the Hartree-Fock level. Molecular bonds tend to have a fairly high degree of ‘covalency’ and the existence of partially-occupied *d* states leads to a great many nearly-degenerate levels, and thus to a large ‘static correlation’ (i.e. the weight of the HF determinant in a CI expansion would be small, and a multi-determinant treatment is more appropriate). Basis sets to describe correlation using quantum chemistry correlated wave function techniques need to be much richer than those for systems well-described at the Hartree-Fock level since they need to treat all of the unoccupied levels. It may seem surprising that single-determinant HF could be so successful in periodic crystalline magnetic insulators containing transition elements, but this is an important characteristic of these *ionic* materials. As we have seen, the highly symmetric environment and long-range Coulomb forces tend to separate the orbitals into well-defined subsets with a significant gap between occupied and unoccupied states. Hence, the ground state of NiO (for example) is rather well described by a single determinant. In this sense, a strongly correlated magnetic insulator is in many ways a ‘simpler system’ than many molecules. The success of UHF calculations in these materials (and also hybrid DFT schemes) has now been well documented in a variety of publications.

In order to study materials containing first and second transition series elements, I carried out an intermittent program of work between 1993 and 1995 aimed at developing entirely new contracted *atomic* basis sets for elements beyond atomic number 20 (Ca). These are not necessarily that good by molecular standards, but in many cases (particularly for the 3*d* elements Sc-Zn) these have since been reoptimized in the solid state and used in published work. These sets are available on the Torino and Cambridge Gaussian basis set library web sites referred to earlier. Since the Torino site has a fairly strict and entirely laudable no paper-no web policy, the atomic basis sets beyond Zn as far as lanthanum including the 4*d* transition elements are largely only available from the Cambridge library. It is encouraging to note however that where these sets have been used in real materials, only relatively minor reoptimizations of the most diffuse functions were required.

Programs

There are two programs (that we have access to) which you can use to optimize basis sets (and incidentally, geometries). Both are Unix shell scripts which work by repeatedly calling CRYSTAL whilst varying the requested basis set/geometry parameters in a CRYSTAL input file. You can do this by hand of course but dying of boredom is, I imagine, rather unpleasant.

Billy

The first and older program was originally written by me in around 1991 (the first program I ever wrote. Aaaah...). For some reason it is called ‘billy’ and it is a Unix csh script. In most respects however, it has been superseded by LoptCG (see below). Billy is very easy to use and is pretty robust, but generally requires more calls to CRYSTAL than LoptCG since it doesn’t use any gradient information in the multidimensional minimization. Rather, it uses repeated line minimizations. Since basis set parameters typically vary only in narrow ranges and roughly keep certain ratios to each other, this is actually not as bad as it sounds and billy usually finds the same minimum as LoptCG (in basis set minimizations anyway), just more slowly. It is actually better at riding over badly behaved input decks where CRYSTAL runs fail to converge for certain values of the parameters. To use it, simply precede any parameter in the CRYSTAL input file you wish to optimize with an asterisk (‘*’) and type something like ‘billy input_filename 5 ‘ where 5 is an initial percentage scan range. See the supplied documentation for additional command line flags for multiple minimization cycles, and for controlling GUESSP restarts. If your calculation is not particularly time-consuming and you don’t want to optimize too many parameters, billy is still perfectly serviceable.
Find billy at : www.tcm.phy.cam.ac.uk/~mdt26/downloads/billy.tar.gz

LoptCG

LoptCG was written in around 1996 by Claudio Zicovich-Wilson whilst working in Torino with the CRYSTAL group, and is now available with the CRYSTAL98 distribution on request. It is a Unix ksh script and is different from billy in that it calculates numerical energy gradients by finite differencing and uses this information to help it carry out a multidimensional conjugate gradient (Polak-Ribiere) minimization. It requires a certain investment of time to learn how to use it properly, and requires more complicated input, but its minimization algorithm is quite a bit more intelligent than billy and I recommend its use. It also has many other nice features such as the ability to change the minimization strategy halfway through an optimization. See the supplied documentation for details. More information about LoptCG is also available at www.ch.unito.it/ifm/teorica/LoptCG.html .

5. Examples[35]

In this final section we shall discuss a few brief but important examples of the effects of basis set selection on the total energy and other related properties. First of all we consider the perovskite $KMnF_3$, described with the basis set reported in Table 5.1. As this system is almost fully ionic, the basis sets for bulk calculations have been derived from basis sets optimized for the isolated K^+, Mn^{2+} and F^- ions. The exponents of the most diffuse single-Gaussian *sp* and *d* shells were reoptimized in the bulk. The basis set in Table 5.1 is expected to be reasonably good - there are three valence *sp* shells on the anion and two on the cation (the 4*s* orbitals of K and Mn are almost completely empty). The *d* electrons are described by two shells, a contraction of four Gaussians for the inner part, and a single Gaussian for the outer part. The calculation with this basis is cheap, taking only a few minutes on a medium-sized workstation. This is because (a) the unit cell contains only five atoms, (b) the system has high symmetry and (c) the external Gaussians of the two cations have reasonably large exponents (0.50 and 0.22 for Mn and K respectively) and that of the anion is not too diffuse (0.18).

The basis set of Table 9 can be improved in a number of ways:

(1) Polarization functions (*d* functions) may be added to the K and F bases.

(2) Additional diffuse *sp* shells can be added to Mn.

(3) the 4-1G contraction for the *d* electrons on Mn can be substituted with a 5-1G.

Some results of these basis set improvements are shown in Table 5.2. The effect both on the run time and in calculations of a number of properties (the binding energy, lattice parameter, bulk modulus, ferro-antiferromagnetic energy difference ΔE, and two elastic constants) are given. Most of these quantities are very stable with respect to basis set improvements, and only in the case of ΔE is a maximum variation of about 20% observed. This stability is a consequence of the fully ionic nature of $KMnF_3$. and of its high symmetry. The electron charge distributions of K^+ and F^- are essentially spherical, so that polarization functions are nearly useless. The 4*sp* shell of Mn is empty and so the additional *sp* shell with exponent 0.25 is not used.

In order to understand the relationship between basis set flexibility, polarizability of the ions and the crystalline symmetry, we will consider the influence of *d* polarization functions on two ionic compounds, Na_2O and K_2O. In Table 5.3 some calculated bulk properties of these materials are reported, obtained with and without *d* functions on the cation. The *d* functions are seen to have negligible influence on all but one of these properties, namely the C_{44} elastic constant, where reductions of 10% and 42% are observed when *d* functions are introduced. These results can be interpreted in the following way. The cations are in a high symmetry position, and when the unit cell is modified according to the deformations required for the evaluation of B, C_{11} and C_{11}–C_{12}, their local symmetry remains cubic. The *d* functions are thus used essentially for describing the ‘breathing’ of the ion. This may also be described by the *s* and *p* functions of the valence shell however. For these quantities the difference between K_2O (with a variation of the order of 3%) and Na_2O (1%) is due to the larger polarizability of the potassium ion, or in other words to the smaller energy difference between the valence *s*/*p* and virtual *d* levels. On the contrary the deformation required for the evaluation of the C_{44} elastic constant drastically reduces the atomic point symmetry. The cation is thus no longer in a centrosymmetric position and the ion can undergo a dipolar relaxation, for which a combination of *p* and *d* functions is required. This effect is less marked for Na_2O, because the sodium ion is less polarizable.

Shell	Mn		K		F	
	exponents	coeffs.	Exponents	coeffs.	exponents	coeffs.
		s(*d*) *p*		*s*(*d*) *p*		*s*(*d*) *p*
s	292601.0	0.000227	172500.0	0.00022	13770.0	0.000877
	42265.0	0.0019	24320.0	0.00192	1590.0	0.00915
	8947.29	0.0111	5140.0	0.01109	326.5	0.0486
	2330.32	0.0501	1343.9	0.04992	91.66	0.1691
	702.047	0.1705	404.5	0.1702	30.46	0.3708
	242.907	0.3691	139.4	0.3679	11.50	0.41649
	94.955	0.4035	54.39	0.4036	4.76	0.1306
	39.5777	0.1437	22.71	0.1459		
sp	732.14	-0.0053 0.0086	402.0	-0.00603 0.0084	19.0	-0.1094 0.1244
	175.551	-0.0673 0.0612	93.5	-0.805 0.0602	4.53	-0.1289 0.5323
	58.5093	-0.1293 0.2135	30.75	-0.0109 0.2117	1.387	1.0 1.0
	23.129	0.2535 0.4018	11.92	0.258 0.3726		
	9.7536	0.6345 0.4012	5.167	0.684 0.4022		
	3.4545	0.2714 0.2222	1.582	0.399 0.186		
sp	38.389	0.0157 -0.0311	17.35	-0.0074 -0.0321	0.44	1.0 1.0
	15.4367	-0.2535 -0.0969	7.55	-0.129 -0.062		
	6.1781	-0.8648 0.2563	2.939	-0.6384 0.1691		
	2.8235	0..9937 1.6552	1.19	1.08 1.5		
			0.674	1.03 1.06		
sp	1.2086	1.0 1.0	0.389	1.0 1.0	0.179	1.0 1.0
sp	0.4986	1.0 1.0	0.216	1.0 1.0		
d	22.5929	0.0708				
	6.1674	0.3044				
	2.0638	0.5469				
	0.7401	0.5102				
d	0.249					
Atom						
sp	=	= =	0.4017	1.0 1.0	=	= =
sp	=	= =	0.2216	1.0 1.0	0.15	1.0 1.0
sp	0.067	1.0 1.0	0.0281	1.0 1.0		

Table 5.1 - Exponents and coefficients of the Gaussian-type basis functions adopted for the study of $KMnF_3$. The first and second part of the table refer to the bulk and atomic basis sets respectively. In the lower part of the table the first two rows give the exponents and coefficients of the functions modified in the atom with respect to the ion in the bulk; the last row refers to the functions added for the description of the atomic tails. The atomic basis set is used for the evaluation of the binding energies given in Table 5.2. The symbol '=' stands for 'unmodified'.

Case	Basis set	N	t	BE	a_0	B	ΔE	C_{44}	C_{11}-C_{12}
a)	Table 5.1	83	1198	0.604	4.280	64.6	0.293	30.9	91.8
b)	5-1*d* not 4-1*d*	83	1409	0.605	4.280	64.1	0.292	30.8	90.9
c)	b) + *sp* Mn(α=0.25)	87	1858	0.606	4.284	63.3	0.334	30.3	91.3
d)	c) + *d* on F (α=0.7)	102	2541	0.608	4.280	63.5	0.319	30.2	89.8
e)	d) + *d* on K (α=0.4)	107	3040	0.609	4.276	63.9	0.325	29.6	94.8

Table 5.2 - Effect of basis set on bulk properties of $KMnF_3$. BE, a_0, ΔE, B, C_{44}, C_{11} and C_{11}–C_{12} are the binding energy (hartree), the lattice parameter (Å), the energy difference between ferromagnetic and antiferromagnetic phases (millihartree), the bulk modulus and two of the elastic constants (GPa). *M* is the number of functions in the basis set; *t* is the total CPU time.

		Na_2O			K_2O	
	no *d*	*d*	Δ%	no *d*	*d*	Δ%
E_T	-398.693	-398.695	-0.002	-1273.184	-1273.193	-0.010
a_0	5.498	5.487	-0.2	6.550	6.466	-1.3
B	58.7	58.7	0.0	33.3	34.6	+3.5
C_{11}	127.3	126.14	-0.9	71.8	74.1	+3.1
C_{12}	23.9	23.8	-0.4	14.2	14.8	+4.1
C_{44}	37.8	34.4	-10.2	19.7	13.9	-41.7

Table 5.3 - Effect on bulk properties of simple oxides of adding *d* polarization functions to the cations. Δ% is the percentage difference between the calculation with and without *d* functions (for E_T it is the absolute difference)

Exercises

1. *Some simple properties of Gaussians*
(a) Compute the overlap integral of two normalized *s*-type Gaussian functions with exponents α and β, and with a common centre.
(b) Compute the overlap integral between two *s*-type functions centred at **A** and **B**, and with exponents α and β respectively.
(c) As (b), but for *p* functions.

NB: Note the following standard integral:

$$\int_0^\infty e^{-\alpha x^2} = \tfrac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

2. *Basis set superposition error (BSSE)*

This exercise is concerned with the evaluation of the counterpoise correction to the basis set superposition error in a simple system, namely CO molecules adsorbed on the (100) surface of MgO. Experimentally, one finds that the CO molecules are vertically adsorbed via the C atom over the Mg ions at the (001) face with an adsorption heat of around 3.6 kcal/mol. Before we do any computations, we must first examine the energetics of surface/adsorbate interactions.

The interaction energy between an ad-molecule *M* and a surface site *S* within a surface complex *MS* is obtained by calculating the total energies of the three systems involved and then finding

$$\Delta E = E(MS) - E(M) - E(S).$$

Each of these quantities must be evaluated at the appropriate equilibrium geometry. Note that the interaction energy is defined to be negative for attractive interactions and that the term ‘binding energy’ refers to the *negative* of the interaction energy. When adsorption layers are treated by periodic methods, as in CRYSTAL, a more specific definition is required in order to take into account the ‘lateral interaction energy’, which is the interaction energy per unit cell between the molecules in their periodic array adsorbed on the surface. This quantity can be either positive (repulsion) or negative (attraction) depending on the nature of the molecules. In the limit of very low coverage the distance between molecules becomes very large and the lateral interaction energy tends to zero.

To compute the binding energy per unit cell per adsorbate molecule the following quantities must therefore be computed:
(1) $E_{\text{slab/ads}}$: the energy per unit cell of a crystal slab with an interacting periodic array of adsorbed molecules.
(2) E_{slab} : the energy per unit cell of the clean crystal slab.

(3) E_{ads} : the energy per unit cell of the periodic array of adsorbed molecules in the absence of the surface.
(4) E_{mol} : the energy of a single isolated adsorbate molecule.

The interaction energy per unit cell between the whole adsorbate layer and the surface is

$$\Delta E_{slab/ads} = E_{slab/ads} - E_{slab} - E_{ads}.$$

The lateral interaction energy is

$$\Delta E_{ads}^{L} = E_{ads} - N \cdot E_{mol}$$

where N is the number of molecules in the unit cell.

The experimental energy of adsorption ΔE_{exp} corresponds to a process where the molecules move from an ideal gas state into an adsorbed state where attractive interactions cause them to become attached to the host surface:

$$\Delta E_{\mathrm{exp}} = E_{slab/ads} - E_{slab} - N \cdot E_{mol}$$

One thus establishes the link between the computed interaction energy and the experimental ΔE_{exp}:

$$\Delta E_{\mathrm{exp}} = \Delta E_{slab/ads} + \Delta E_{ads}^{L}$$

In the limit of low coverage, this is effectively

$$\Delta E_{\mathrm{exp}} \approx \Delta E_{slab/ads}$$

So anyway, having calculated this quantity, we might suspect that basis set superposition error has affected the result. This error arises in the following way. As the basis sets used in the calculation are generally far from complete, both the adsorbate layer and the surface layer may use the additional variational freedon offered by each others basis functions to lower their energy. This gives a non-physical, stabilizing contribution to the energy of the surface-adsorbate complex, and may also lead to artificial charge transfer if the basis set description of the two subsytems is unbalanced. Hence there may be an error in the interaction energy which is connected with the superposition of the basis functions of the two subsystems.

The stability of the result with respect to this error may be checked by the *counterpoise correction*. To do this one must recalculate E_{slab} and E_{ads} supplementing the basis set of each subsystem with all the basis functions of the other but without their electrons and nuclei. These additional basis functions are referred to as ‘ghost functions’. The energies obtained at the equilibrium geometry of the complex for each subsystem e.g. $E(M\{S\})$ are lower than the energies calculated at the same geometry with the basis functions of the respective subsystems alone e.g. $E(M)$, and the difference ε is defined as the BSSE:

$$\varepsilon(M) = E(M) - E(M\{S\})$$

$$\varepsilon(S) = E(S) - E(S\{M\})$$

The BSSE values $\varepsilon(M)$ and $\varepsilon(S)$ are then used to define a counterpoise-corrected interaction energy

$$\Delta E^{c}_{\mathrm{exp}} = \Delta E_{\mathrm{exp}} + \varepsilon(M) + \varepsilon(S).$$

This quantity should always be calculated as a check of the quality and balance of the basis set.

In CRYSTAL, the counterpoise correction for such a surface/adsorbate system is calculated using the GHOSTS option, by means of which selected atoms may be turned into ‘ghosts’ by deleting their nuclear and electronic charges, and setting their conventional atomic number to zero.

Prepare input files for the following (using basis set libraries and appropriate defaults)

mgo_co:	single layer MgO slab with adsorbed CO molecules.
mgo_ghost:	single layer MgO slab with ghost CO basis functions.
co:	periodic array of CO atoms without MgO slab (real or ghost).
co_ghost:	periodic array of CO molecules with ghost MgO basis functions.
co_mol:	single isolated CO molecule.
mgo:	single layer MgO slab

The geometry for the MgO(100)+adsorbed CO system may be specified in CRYSTAL format as follows (you should be able to work out all other geometries using this example):

```
CRYSTAL
0 0 0
225
4.21
2
12      0.0 0.0 0.0
8       0.5 0.5 0.5
SLAB
0 0 1
1 1
BREAKSYM
ATOMINSE
2
6       1.488 –1.488 4.605
108     1.488 –1.488 5.729
ENDG
```

Can you explain why we use 108 for the atomic number of oxygen when adding the CO molecule? Now modify the inputs containing CO molecules using the SUPERCELL option to ensure an adsorbate coverage of one half, that is, half the magnesium ions on the surface have an adsorbed CO molecule. Run CRYSTAL

Hartree-Fock calculations from your six files. They should run very quickly. Note the total energies of these six calculations.

(a) Calculate the interaction energy (kcal/mol) per unit cell between the MgO surface and the CO overlayer $\Delta E^{cell}_{slab/ads}$, ignoring BSSE. Is the interaction attractive or repulsive?
(b) Calculate the lateral interaction energy. Do the CO molecules on the surface attract or repel each other? Hence correct the interaction energy of adsorption to form the quantity ΔE_{exp} which may be meaningfully compared with experiment. The experimental heat of adsorption is –3.6 kcal/mol. How well are we doing?
(c) Compute the counterpoise correction to ΔE_{exp}. What is the magnitude and sign of the counterpoise-corrected interaction energy? How big is the BSSE compared to the uncorrected interaction energy?
(d) Repeat the whole exercise using *a posteriori* correlation corrections to the Hartree-Fock energy using the PWGGA functional, and also regular DFT with the PWGGA functional. How do the results compare with experiment and each other? How would you suggest the calculations presented here (which are reasonably crude) might be improved?

NB: To avoid typing mistakes on calculators, it is better to copy energies onto the Unix calculator with the mouse and do the sums with that (type 'bc -l' to get the calculator).
Also, to convert from Hartree to kcal/mol multiply by 627.50754.

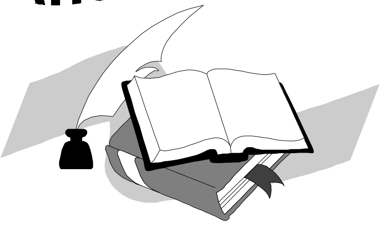
3. *Basis set development and computation of properties in lithium metal*

Read again the description of the lithium metal calculations of Doll, Harrison and Saunders in section 5 of the notes (originally reported in Ref. 24). Prepare CRYSTAL input files for bulk Li using the three basis sets specified (noting also the details of the reciprocal space sampling and auxiliary basis sets, and using sensible defaults for the rest of the input parameters). Prepare an input file also for atomic lithium using the suggested Li atomic set. See if you can come up with ways of improving these basis sets (you might familiarize yourself with the optimizer scripts *billy* and/or *LoptCG* while you're at it) and examine how these 'improvements' affect the CPU time. Calculate some simple bulk properties of your choice (suggestions: lattice constant, bulk modulus, cohesive energy, surface energies.) and see how they change using different Hamiltonians (HF and different DFT functionals) and the various basis sets (including your 'improved' one). Ask for the experimental values when you've finished.

Note that the geometry of bulk Li can be specified in CRYSTAL format as follows:

```
CRYSTAL
0 0 0
229
3.44
1
3 0.0 0.0 0.0
ENDG
```

Answers



1(a). A useful property of Gaussian functions is that the product of Gaussians are other Gaussians, and also that so many integrals factorize. In cases like this, we use

$$e^{-\alpha \mathbf{r}^2} e^{-\beta \mathbf{r}^2} = e^{-(\alpha+\beta)\mathbf{r}^2}$$

to convert to a single Gaussian, and combine with the formula

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\alpha \mathbf{r}^2} dxdydz = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx \int_{-\infty}^{\infty} e^{-\alpha y^2} dy \int_{-\infty}^{\infty} e^{-\alpha z^2} dz = \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}}$$

Including real normalization constants N_1 and N_2, we get

$$\langle \phi_1 | \phi_1 \rangle = N_1^2 \left(\frac{\pi}{2\alpha}\right)^{\frac{3}{2}} = 1$$

$$\langle \phi_2 | \phi_1 \rangle = N_1 N_2 \left(\frac{\pi}{\alpha+\beta}\right)^{\frac{3}{2}}$$

$$\langle \phi_2 | \phi_2 \rangle = N_2^2 \left(\frac{\pi}{2\beta}\right)^{\frac{3}{2}} = 1$$

Eliminating, we find

$$\langle \phi_2 | \phi_1 \rangle = 2^{\frac{3}{2}} \frac{(\alpha\beta)^{\frac{3}{4}}}{(\alpha+\beta)^{\frac{3}{2}}} = \left(\frac{\sqrt{\alpha\beta}}{(\alpha+\beta)/2}\right)^{\frac{3}{2}}$$

The fraction in parentheses in the last expression on the RHS is the ratio of the geometric average to the arithmetic average of the positive numbers α and β. This is less than 1, except when the numbers are equal, and then it is 1.

(b) Another useful fact is that the product of two Gaussians is a new Gaussian, even if they are not on the same centre.

To show this, we first need the fact that

$$\alpha(x-A)^2 + \beta(x-B)^2 = (\alpha+\beta)x^2 - 2(\alpha A + \beta B)x + \alpha A^2 + \beta B^2 = (\alpha+\beta)(x-C)^2 + D$$

which is easily solved to give $C = \frac{\alpha A + \beta B}{\alpha + \beta}$ and $D = \frac{\alpha\beta}{\alpha + \beta}(A - B)^2$. This implies that

$$N_1 e^{-\alpha(\mathbf{r}-\mathbf{A})^2} N_2 e^{-\beta(\mathbf{r}-\mathbf{B})^2} = N_1 N_2 e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} e^{-\gamma(\mathbf{r}-\mathbf{C})^2}$$

with $\gamma = \alpha + \beta$. For *s* functions, the overlap integral is thus

$$S = N_1 N_2 e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} \left(\frac{\pi}{\gamma}\right)^{\frac{3}{2}}$$

With the known normalization factors from (a), we finally obtain

$$S = \left(\frac{\sqrt{\alpha\beta}}{(\alpha+\beta)/2}\right)^{\frac{3}{2}} e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2}$$

which is also obvious from the solution of part (a). Note that the new centre $\mathbf{C} = \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\alpha + \beta}$ is simply the weighted mean of the original centres.

(c) From the previous solution, it is obvious we can now generalize:

$$\phi_1 = N_1 p_1(\mathbf{r} - \mathbf{A}) e^{-\alpha(\mathbf{r}-\mathbf{A})^2}$$

$$\phi_2 = N_2 p_2(\mathbf{r} - \mathbf{B}) e^{-\beta(\mathbf{r}-\mathbf{B})^2}$$

$$\Rightarrow$$

$$\phi_1\phi_2 = N_1 N_2 F p(\mathbf{r} - \mathbf{C}) e^{-\gamma(\mathbf{r}-\mathbf{C})^2}$$

where p_1 is a polynomial of total degree n_1, expressing the angular dependence around centre **A**, p_2 has total degree n_2 around centre **B**, and

$$\mathbf{C} = \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\alpha + \beta}$$

$$F = \exp\left(-\frac{\alpha\beta}{\alpha + \beta}(\mathbf{A} - \mathbf{B})^2\right)$$

$$\gamma = \alpha + \beta$$

In particular, for two *sp* shells, we obtain $x - A_x = (x - C_x) + (C_x - A_x)$ etc., so

$$(x-A_x)(x-B_x)=(x-C_x)^2-2(x_{CA}+x_{CB})(x-C_x)+x_{CA}x_{CB}$$

and so on, where x_{CA} is short for C_x–A_x etc. The following integrals are standard:

$$I_0=\iiint \exp(-\gamma(\mathbf{r}-\mathbf{C})^2)d\upsilon=\left(\frac{\pi}{\gamma}\right)^{\frac{3}{2}}$$

$$I_2=\iiint (x-C_x)^2\exp(-\gamma(\mathbf{r}-\mathbf{C})^2)d\upsilon=\left(\frac{1}{2\gamma}\right)\left(\frac{\pi}{\gamma}\right)^{\frac{3}{2}}=\frac{I_0}{2\gamma}$$

The overlap integrals are thus

$$S=N_1N_2F\times\begin{pmatrix} I_2+x_{CA}x_{CB}I_0 & x_{CA}y_{CB}I_0 & x_{CA}z_{CB}I_0 \\ y_{CA}x_{CB}I_0 & I_2+y_{CA}y_{CB}I_0 & y_{CA}z_{CB}I_0 \\ z_{CA}x_{CB}I_0 & x_{CA}y_{CB}I_0 & I_2+z_{CA}z_{CB}I_0 \end{pmatrix}$$

This is an important general point. All the integrals involving the various components of complete shells of Cartesian (or spherical harmonic) Gaussians are obtained from a few values in common for all integrals, combined with simple expressions involving the relative co-ordinates of the centre.

2. *Adsorption of CO on the MgO (001) surface.*

This is what I get in the HF and a posteriori PWGGA cases (you will have to do pure DFT PWGGA yourself..).
(energy units Hartree unless otherwise stated)

STANDARD HARTREE-FOCK TREATMENT

total energies:

CO	–112.6265204421
CO with MgO ghost	–112.6287274346
MgO	–549.2096009758
MgO with CO ghost	–549.2153973595
MgO with adsorbed CO	–661.8392701443
interaction energy per unit cell ($E_{\mathrm{slab/ads}}$)	–0.0031487264
i.e.	–1.976 kcal/mol (attractive)

lateral interaction energy

energy of isolated CO molecule	–112.6270474548
energy of CO layer with no MgO	–112.6265204421
lateral interaction energy ΔE_{ads}^{L}	+0.0005270127 (repulsive)

[Note this is half coverage - for full coverage, a ΔE_{ads}^{L} of +0.00624 - twelve times higher - was obtained]

Therefore ΔE_{exp} is	–0.0026217137
i.e.	–1.645 kcal/mol (attractive)

which may be compared with around –3.6 kcal/mol experimentally. Not too bad. However,

counterpoise correction:

ε(CO)	+0.0022069925
ε(MgO)	+0.0057963837
Therefore total BSSE	+0.0080033762
Counterpoise-corrected energy $\Delta E^{c}_{\exp}$	+0.0053816625 (repulsive)

Therefore *all* the binding observed in the original calculation was due to basis set superposition error. Such a calculation using CRYSTAL, ignoring BSSE, was published in 1986. It seems we must improve our treatment. For such a weak bond, correlation may be important. One way to improve the results could therefore be to estimate *correlation-corrected* interaction energies using density functionals of the Hartree-Fock density:

A POSTERIORI CORRELATION

correlation-corrected total energies:

CO	–113.116080
CO with MgO ghost	–113.117780
MgO	–550.756528
MgO with CO ghost	–550.760809
MgO with adsorbed CO	–663.882652
interaction energy per unit cell ($E_{\text{slab/ads}}$)	–0.010044
i.e.	–6.302 kcal/mol (attractive)

lateral interaction energy

energy of isolated CO molecule	–113.116612
energy of CO layer with no MgO	–113.116080
lateral interaction energy ΔE^{L}_{ads}	+0.000532(repulsive)
Therefore $\Delta E_{\exp}$ is	–0.009512
i.e.	–5.968 kcal/mol (attractive)

counterpoise correction:

ε(CO)	+0.001700
ε(MgO)	+0.004281
Therefore total BSSE	+0.005981
Counterpoise-corrected energy $\Delta E^{c}_{\exp}$	–0.003531 (attractive)
i.e.	–2.215 kcal/mol

to be compared with around –3.6 kcal/mol experimentally. This is a reasonable result. It suggests that much of the binding for CO on MgO is due to correlation effects beyond the Hartree-Fock level. Of course however, we have no reason to expect such good agreement since we are still using a rather poor model, and the next correction may shift the answer considerably and in the wrong direction. We should probably investigate:

(a) Use of better basis sets on all atoms.
(b) Slabs thicker than one layer.
(c) Rumpling of slabs at the surface.
(d) Careful optimization of CO bond length and position above surface.
(e) More sophisticated correlation treatments than correlation-corrected Hartree-Fock – quantum Monte Carlo being a good bet!

3. There aren't any right answers to this exercise. Just get some hands on experience at playing with input files and running CRYSTAL/billy/LoptCG.

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[35] This section is based on work done by R. Dovesi and F. Freyria-Fava, and the text, apart from certain grammatical aspects, is largely reproduced from RD’s notes on ‘Total Energy and Related Properties’ from the 1995 Torino Summer School.